

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-237927

(43)Date of publication of application : 09.09.1997

(51)Int.Cl.

H01L 51/00  
C23C 18/08  
H01L 21/20  
H01L 21/368  
H01L 31/04

(21)Application number : 08-247869

(71)Applicant : TOSHIBA CORP

(22)Date of filing : 19.09.1996

(72)Inventor : BEPPU TATSURO  
HAYASE SHUJI  
HIRAOKA TOSHIRO  
KAMATA ATSUSHI  
SANO KENJI

(30)Priority

Priority number : 07338877  
07338940

Priority date : 26.12.1995  
26.12.1995

Priority country : JP

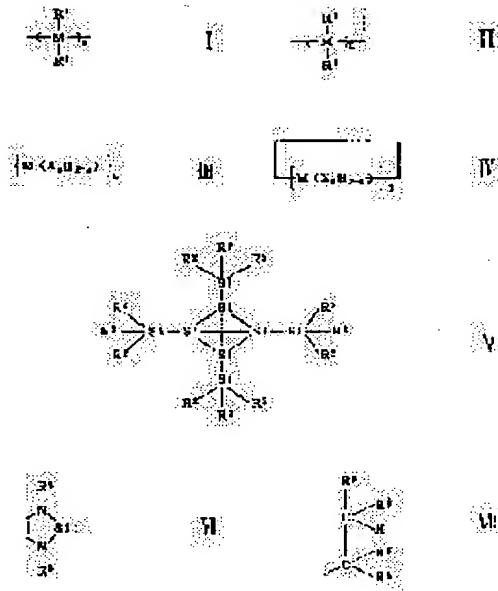
JP

## (54) SEMICONDUCTOR FILM FORMING METHOD AND SOLAR CELL MANUFACTURING METHOD

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To easily form a Si or Ge semiconductor film having a large area by selecting a semiconductor material from among compds. expressed by specified formulae.

**SOLUTION:** A semiconductor material is selected from among compds. given by formulae I, II (M is Si or Ge, R1 selected among H and alkyls having 2C or more and beta H), III, IV (X is halogen atom, n is 4 or higher integer, a is 1 or 1) V (R2 is substituted group given by VII nonsubstituted alkyl group, R3 is H atom, 1-15C substituted group, R4 is 1-15C substituted group) VI (R5 is 1-15C substituted group) to form a semiconductor thin film. This soln. is coated and thermally decomposed to form a Si film having a large area.



### LEGAL STATUS

[Date of request for examination]

30.03.2001

[Date of sending the examiner's decision of

[rejection]

[Kind of final disposal of application other than  
the examiner's decision of rejection or  
application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision  
of rejection]

[Date of requesting appeal against examiner's  
decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

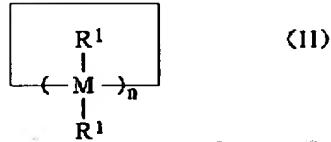
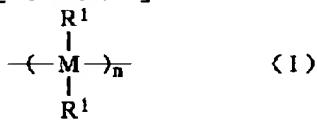
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## CLAIMS

## [Claim(s)]

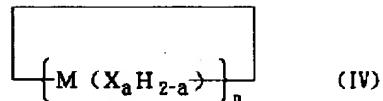
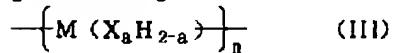
[Claim 1] General formula (I) After applying the solution of a semi-conductor raw material on a substrate, it is the approach of pyrolyzing, separating a semi-conductor and forming a semi-conductor thin film, and said semi-conductor raw material reaches (II).

## [Formula 1]



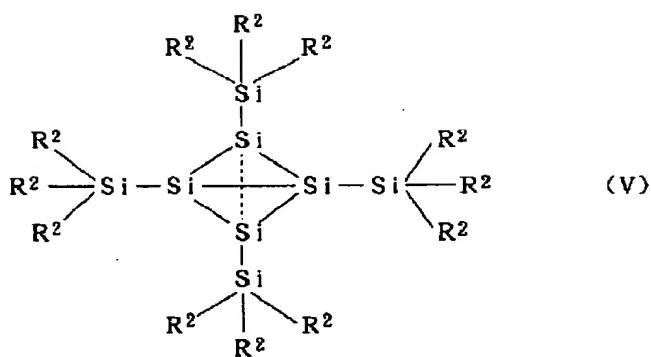
(— M is chosen from the group which consists of silicon and germanium among a formula, and R1 is independently chosen from the group which consists of hydrogen, a with a carbon numbers of two or more in which at least beta has hydrogen alkyl group and a phenyl group, and a silyl radical, respectively. ) — the compound and general formula (III) which are expressed — and (VI)

## [Formula 2]



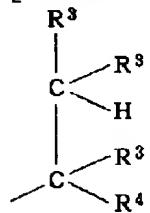
(— M is chosen from the group which consists of silicon and germanium among a formula, and X is [ four or more integers and a of a halogen atom and n ] 1 or 2.) — the compound and general formula (V) which are expressed

## [Formula 3]



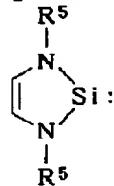
(R2 is independently chosen from the group which consists of the permutation expressed with the following type or an unsubstituted alkyl group, an aryl group, and an aralkyl radical among a formula, respectively.)

[Formula 4]



the inside of a formula, and R3 — respectively — independent — the permutation of a hydrogen atom and carbon numbers 1–15, or an unsubstituted alkyl group — It is chosen from the group which consists of the permutation or unsubstituted aralkyl radical of the permutation of carbon numbers 6–15 or an unsubstituted aryl group, and carbon numbers 7–15. R4 It is chosen from the group which consists of the permutation or unsubstituted aralkyl radical of the permutation of the permutation of carbon numbers 1–15 or an unsubstituted alkyl group, and carbon numbers 6–15 or an unsubstituted aryl group, and carbon numbers 7–15. The compound expressed and a general formula (VI)

[Formula 5]



(— R5 is independently chosen from the group which consists of a permutation or an unsubstituted silyl radical with the permutation of carbon numbers 1–15 or an unsubstituted alkyl group, an aryl group, an aralkyl radical, and 1–5 silicon among a formula, respectively.) — the semi-conductor thin film formation approach characterized by being chosen from the group which consists of a compound expressed.

[Claim 2] Said general formula (I) The semi-conductor thin film formation approach characterized by separating the semi-conductor which pyrolyzes and contains the impurity of a predetermined conductivity type after adding the source of a dopant which gives the conductivity type of p mold or n mold to the solution of the semi-conductor raw material chosen from the group which consists of a compound expressed with — (VI) and applying on a substrate.

[Claim 3] Said general formula (I) The semi-conductor thin film formation approach characterized by separating the semi-conductor which pyrolyzes in the ambient atmosphere containing the source of a dopant which gives the conductivity type of p mold or n mold, and contains the impurity of a predetermined conductivity type after applying on a substrate the solution of the semi-conductor raw material chosen from the group which consists of a compound expressed with — (VI).

[Claim 4] In manufacturing the solar battery which prepared the semi-conductor thin film which has one of conductivity types among i mold, p mold, and n mold more than two-layer in inter-electrode [ one pair of ], and formed semi-conductor junction in it In forming the semi-conductor thin film of i mold, after applying the solution of the semi-conductor raw material chosen from the group which consists of a compound expressed with said general formula (I) – (VI), In adopting the process which it pyrolyzes [ process ] and separates a semi-conductor and forming the semi-conductor thin film of p mold or n mold Said general formula (I) [ whether it pyrolyzes, after adding the source of a dopant which gives a predetermined conductivity type to the solution of the semi-conductor raw material chosen from the group which consists of a compound expressed with – (VI) and applying on a substrate, and ] Or by pyrolyzing in the ambient atmosphere containing the source of a dopant which gives a predetermined conductivity type after applying on a substrate the solution of the semi-conductor raw material chosen from the group which consists of a compound expressed with said general formula (I) – (VI) The manufacture approach of the solar battery characterized by adopting the process which separates the semi-conductor containing the impurity which gives a predetermined conductivity type, repeating these processes, and forming the semi-conductor thin film more than two-layer.

---

[Translation done.]

## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of a solar battery of having used the new semi-conductor thin film formation approach and this approach.

[0002]

[Description of the Prior Art] Conventionally, as an approach of forming the semi-conductor thin film which consists of the silicon or germanium which is IV group element, vapor growth, such as vacuum deposition, a spatter, the ion plating method, and a CVD method, is used. However, in order that each of these approaches might use a reduced pressure environment, a hydrogen furnace environment, etc. at the time of membrane formation, it was indispensable to have used an airtight high reaction container, and they was difficult to form a uniform semi-conductor thin film on the substrate of a large area. For this reason, there was a limitation in manufacturing what has a single or more large figures area by the conventional ratio with the application product which has a semi-conductor thin film, for example, a solar battery.

[0003] Then, it considers using the wet applying method as one of the approaches of forming the semi-conductor thin film of a large area. For example, the approach of forming a silicon thin film is indicated by JP,4-119996,A by applying compounds, such as OKUTASHIRA cubane, as a source of silicon on a substrate, and pyrolyzing this source compound of silicon. This approach does not need a large-scale and expensive manufacturing facility like a vacuum chamber, but it is thought that it is advantageous to forming a silicon thin film easily on the substrate of a large area.

[0004] However, to oxygen, compounds, such as OKUTASHIRA cubane indicated by this official report, have many unstable things, in air, oxidize easily and denaturalize. Moreover, these compounds have that the solubility to a solvent is [ much ] low, and are difficult to form a uniform thin film.

[0005] Furthermore, if the application to a solar battery etc. is taken into consideration, it is necessary to form the silicon thin film which doped the impurity of p mold or n mold. However, conventionally, since the impurity was doped by thermal diffusion or the ion implantation after forming a silicon thin film by the pyrolysis, large-scale equipment was needed and complication of a process had been caused.

[0006]

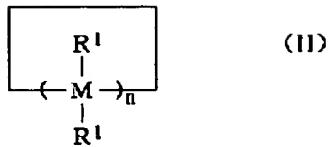
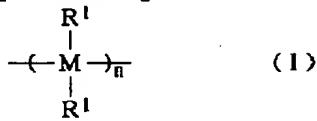
[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the approach of forming easily the semi-conductor thin film which consists of the silicon or germanium of a large area, and the method of manufacturing the solar battery of a large area using this approach.

[0007]

[Means for Solving the Problem] General formula (I) After the semi-conductor thin film formation approach of this invention applies the solution of a semi-conductor raw material on a substrate, it is the approach of pyrolyzing, separating a semi-conductor and forming a semi-conductor thin film, and said semi-conductor raw material reaches (II).

[0008]

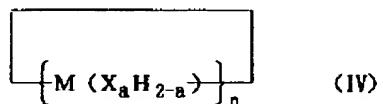
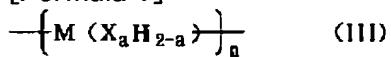
## [Formula 6]



(— M is chosen from the group which consists of silicon and germanium among a formula, and R1 is independently chosen from the group which consists of hydrogen, a with a carbon numbers of two or more in which at least beta has hydrogen alkyl group and a phenyl group, and a silyl radical, respectively.) — the compound and general formula (III) which are expressed — and (IV)

[0009]

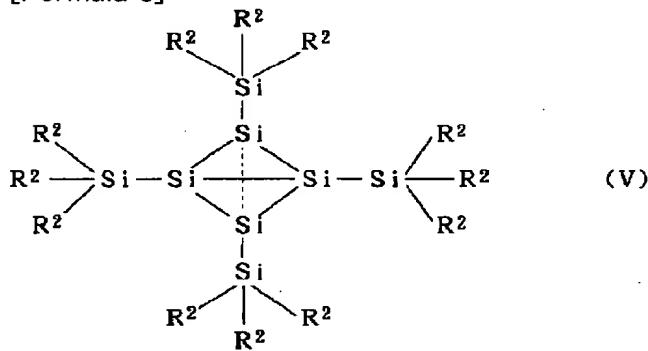
## [Formula 7]



(— M is chosen from the group which consists of silicon and germanium among a formula, and X is [ four or more integers and a of a halogen atom and n ] 1 or 2.) — the compound and general formula (V) which are expressed

[0010]

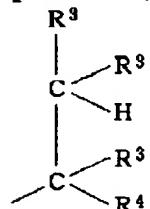
## [Formula 8]



(R2 is independently chosen from the group which consists of the permutation expressed with the following type or an unsubstituted alkyl group, an aryl group, and an aralkyl radical among a formula, respectively.)

[0011]

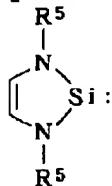
## [Formula 9]



the inside of a formula, and R3 — respectively — independent — the permutation of a hydrogen atom and carbon numbers 1–15, or an unsubstituted alkyl group — It is chosen from the group which consists of the permutation or unsubstituted aralkyl radical of the permutation of carbon numbers 6–15 or an unsubstituted aryl group, and carbon numbers 7–15. R4 It is chosen from the group which consists of the permutation or unsubstituted aralkyl radical of the permutation of the permutation of carbon numbers 1–15 or an unsubstituted alkyl group, and carbon numbers 6–15 or an unsubstituted aryl group, and carbon numbers 7–15. The compound expressed and a general formula (VI)

[0012]

[Formula 10]



(— R5 is independently chosen from the group which consists of a permutation or an unsubstituted silyl radical with the permutation of carbon numbers 1–15 or an unsubstituted alkyl group, an aryl group, an aralkyl radical, and 1–5 silicon among a formula, respectively.) — it is chosen from the group which consists of a compound expressed.

[0013] After the formation approach of a semi-conductor thin film in this invention of having a predetermined conductivity type adds the source of a dopant which gives the conductivity type of p mold or n mold to the solution of the semi-conductor raw material chosen from the group which consists of a compound expressed with said general formula (I) – (VI) and applies it on a substrate, it separates the semi-conductor which pyrolyzes and contains the impurity of a predetermined conductivity type.

[0014] Other formation approaches of a semi-conductor thin film in this invention of having a predetermined conductivity type separate the semi-conductor which pyrolyzes in the ambient atmosphere containing the source of a dopant which gives the conductivity type of p mold or n mold, and contains the impurity of a predetermined conductivity type, after applying on a substrate the solution of the semi-conductor raw material chosen from the group which consists of a compound expressed with said general formula (I) – (VI).

[0015] In the manufacture approach of the solar battery of this invention manufacturing the solar battery which prepared the semi-conductor thin film which has one of conductivity types among i mold, p mold, and n mold more than two-layer in inter-electrode [ one pair of ], and formed semi-conductor junction in it In forming the semi-conductor thin film of i mold, after applying on a substrate the solution of the semi-conductor raw material chosen from the group which consists of a compound expressed with said general formula (I) – (VI), In adopting the process which it pyrolyzes [ process ] and separates a semi-conductor and forming the semi-conductor thin film of p mold or n mold Said general formula (I) [ whether it pyrolyzes, after adding the source of a dopant which gives a predetermined conductivity type to the solution of the semi-conductor raw material chosen from the group which consists of a compound expressed with – (VI) and applying on a substrate, and ] Or by pyrolyzing in the ambient atmosphere containing the source of a dopant which gives a predetermined conductivity type after applying on a substrate the solution of the semi-conductor raw material chosen from the group which consists of a compound expressed with said general formula (I) – (VI) The process which separates the semi-conductor containing the impurity which gives a predetermined conductivity type is adopted, these processes are repeated, and the semi-conductor thin film more than two-layer is formed.

[0016]

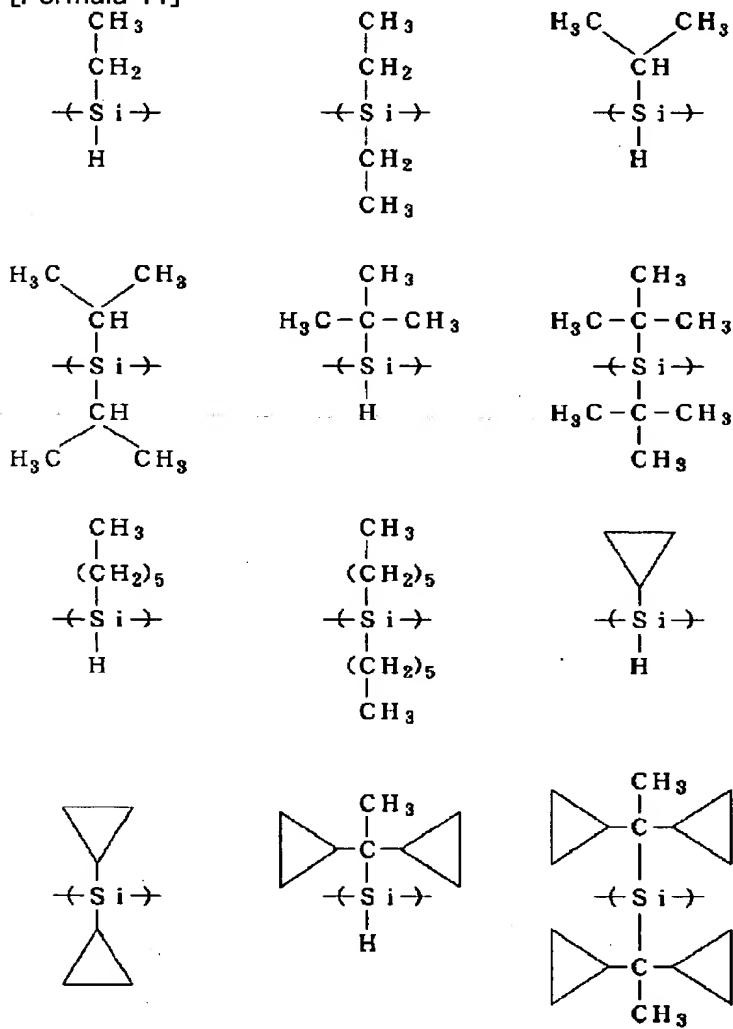
[Embodiment of the Invention] Hereafter, this invention is further explained to a detail. In this invention, the ingredient of the arbitration chosen from semi-conductors, such as silicon, glass, the glass that has a transparent electrode, a metal, the ceramics, a thermally stable polymer, etc. as a substrate ingredient can be used.

[0017] The compound used as the semi-conductor raw material used in this invention is explained. The compound expressed with a general formula (I) or (II) is the silane system which makes a single dimension chain or cyclic structure, or a germane system compound. A copolymer is sufficient as these compounds and they may be used as mixture. In this invention, it is a solid-state at a room temperature, and a meltable compound is used for an organic solvent. In order to fulfill such conditions, it is desirable that polymerization degree  $n$  is 10000 or less [ 3 or more ] in the polymer which has for example, single dimension chain structure, and it is more desirable to a pan that it is 5-30.

[0018] The example of a compound expressed with a general formula (I) or (II) is shown below. In addition, although only the polysilane of a single dimension chain is shown below, annular polysilane is sufficient and, of course, the poly germane who transposed silicon to germanium is sufficient.

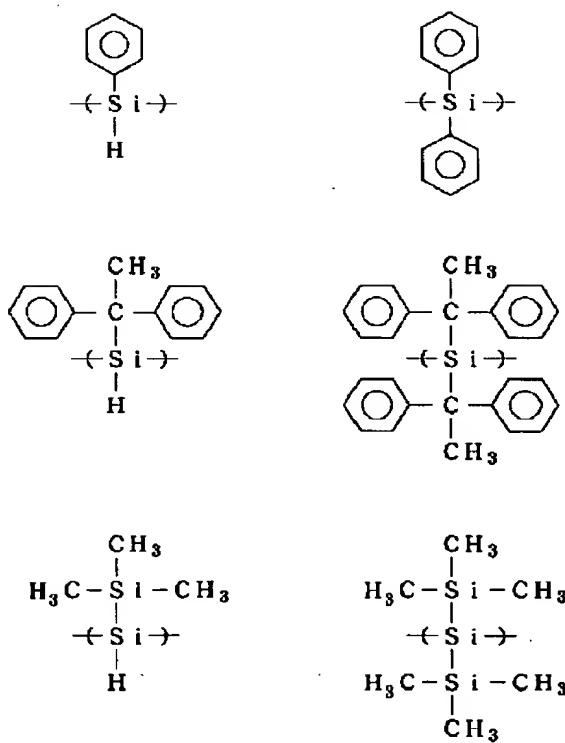
[0019]

[Formula 11]



[0020]

[Formula 12]



[0021] The compound expressed with a general formula (III) or (IV) is a halogenide of silicon or/and germanium. In order to fulfill the conditions of being meltable, to an organic solvent, as for these halogenides, it is desirable that weight average molecular weight is 500–100,000. Since it volatilizes from a substrate before a pyrolysis will happen, if molecular weight is small, the good film is hard to be formed. If molecular weight is the above-mentioned range, the vapor pressure in pyrolysis temperature is comparatively low, and the volatilization from a substrate can be disregarded. If molecular weight is too large, the solubility over a solvent will fall and spreading to a substrate will become difficult.

[0022] It is a solid-state at a room temperature, and the silane system compound expressed with a general formula (V) is meltable to an organic solvent, and its stability over oxidation is high. It is a solid-state at a room temperature, and the silylene compound expressed with a general formula (VI) is meltable to an organic solvent, and its stability over oxidation is high.

[0023] Since the compound expressed with general formula (I) – (VI) used in this invention is meltable to an organic solvent, it is applied on the substrate which has the flat surface or curved surface of a large area by the method of applying arbitration, such as dipping, spin coating, and spray coating, and can form a uniform paint film. As for the thickness of a paint film, it is desirable that it is dozens of nm. The instrument used at this spreading process can be chosen as arbitration according to the magnitude of a substrate. Moreover, if atmospheric mixing can be prevented about a coater, it is enough and a large-scale airtight high decompression device like [ in the case of vapor growth ] is unnecessary.

[0024] In this invention, after heating the paint film of the compound applied on the substrate before and behind the melting point in reducing atmospheres, such as a predetermined ambient atmosphere, for example, an inert gas ambient atmosphere, or hydrogen, and evaporating a solvent, by making a pyrolysis reaction cause, silicon or/and germanium are separated and a semi-conductor thin film is formed. The pressure of an ambient atmosphere is good before and behind ordinary pressure (one atmospheric pressure). Moreover, as for a resultant, removing with exhaust air is desirable. Especially a heating means may not be limited, but may use a common electric furnace, may irradiate infrared radiation like the rapid thermal annealing method, and may perform laser annealing. Concrete pyrolysis temperature changes with compounds. For example, in the case of the compound expressed with a general formula (I) and (II), it is desirable to carry out a pyrolysis at 200–700 degrees C and further 300–650 degrees C. In the case of the

compound expressed with a general formula (III) and (IV), a pyrolysis happens in about 250 degrees C – about 1300 degrees C, but it is desirable to carry out a pyrolysis at 300–500 degrees C. In the case of the compound expressed with a general formula (V) and (VI), it is desirable to carry out a pyrolysis at 300–700 degrees C. A programming rate is set as 5 degrees C / min extent. Reaction time is enough in 10 minutes – 10 hours. However, a temperature up may not be carried out depending on the case, but the pyrolysis in constant temperature may be performed.

[0025] By this pyrolysis reaction, the elimination reaction of the substituent introduced into the side chain of a semi-conductor raw material occurs. For example, a beta elimination reaction occurs with the compound which has a with a carbon numbers of two or more in which at least beta has hydrogen alkyl group, and radical desorption happens with the compound which has a phenyl group. Silicon or the polycrystal thin film of germanium can be formed by such pyrolysis reaction. Moreover, decomposition by UV irradiation is used together, and if pyrolysis temperature is reduced, an amorphous thin film can be formed. In addition, these thin films contain some hydrogen in addition to IV group element.

[0026] The mixed semi-conductor thin film of silicon and germanium can also be formed by applying and carrying out the pyrolysis of the solution of the mixture of a silane system compound and a germane system compound, or the solution of the copolymer which has the repeat unit of a silane, and germane's repeat unit. In addition, for controlling a presentation with silicon and germanium, the former approach is more desirable.

[0027] The equipment for enforcing the approach of above this inventions is typically shown in drawing 1 – drawing 3. As shown in drawing 1 (a), in order to put in a substrate 1 in the coater 3 equipped with the nozzle 4 and to prevent atmospheric-air mixing into a coater 3, after considering as nitrogen-gas-atmosphere mind, the solution of a semi-conductor raw material is sprayed from a nozzle 4, and it applies on a substrate 1. In this case, the amount of the solution applied on a substrate 1 is controllable by setting up nozzle dimensions and spraying time amount suitably. Next, as shown in drawing 1 (b), the substrate 1 with which the solution of a semi-conductor raw material was applied is put into the hydrogen furnace 5, a substrate 1 is heated at a heater 6 in the reducibility gas ambient atmosphere which makes hydrogen a subject, the pyrolysis of the semi-conductor raw material is carried out, and the semi-conductor thin film 2 is formed on a substrate 1. In addition, an infrared heater, a resistance heating heater, etc. can be used as a heater 6.

[0028] As shown in drawing 2, a substrate 1 is put in in the hydrogen furnace 5, and the solution of a semi-conductor raw material can be directly sprayed from a nozzle 4 on a substrate 1, it can apply on a substrate 1, a substrate 1 can be heated at a heater 6, and a semi-conductor thin film can also be formed by pyrolyzing a semi-conductor raw material.

[0029] Moreover, drawing 3 shows the equipment for manufacturing a semi-conductor thin film continuously using a flexible substrate. The flexible substrate 1 is supplied from a supply roll 11, and it is immersed in the semi-conductor raw material solution 8 in the raw material container 7. A substrate 1 is sent to the hydrogen furnace 5 with the delivery rolls 12 and 12. It is heated at a heater 6 in the hydrogen furnace 5, the pyrolysis of a semi-conductor raw material is performed, and a semi-conductor thin film is formed on a substrate 1. Then, a substrate 1 is rolled round and rolled round by the roll 13. Thus, a semi-conductor thin film can be continuously formed on a flexible substrate.

[0030] In this invention, the semi-conductor thin film of a predetermined conductivity type can also be formed by using the source of a dopant which gives the conductivity type of p mold or n mold. The two following approaches can be used as the approach. Namely, after adding the source of a dopant which gives the conductivity type of p mold or n mold to the solution of the semi-conductor raw material chosen from the group which consists of a compound expressed with (1) general-formula (I) – (VI) and applying on a substrate, How to separate the semi-conductor which pyrolyzes and contains the impurity of a predetermined conductivity type, And after applying on a substrate the solution of the semi-conductor raw material chosen from the group which consists of a compound expressed with (2) general-formula (I) – (VI), It is the approach of separating the semi-conductor which pyrolyzes in the ambient atmosphere

containing the source of a dopant which gives the conductivity type of p mold or n mold, and contains the impurity of a predetermined conductivity type. The equipment and the reaction condition for enforcing these approaches are the same with having indicated previously, and good.

[0031] In these approaches, generally, boron (B) is used as a p mold impurity, and Lynn (P), an arsenic (As), and antimony (Sb) are used as an n mold impurity. By the approach of (1), the alkylation object of an impurity element or the compound which has association with an impurity element and Si in intramolecular is used as a source of a dopant. By the approach of (2), the alkylation object of an impurity element, the compound which has association with an impurity element and Si in intramolecular, or the hydride of an impurity element is used as a source of a dopant. Although the addition of the source of a dopant to a semi-conductor raw material is based on high impurity concentration required for the semi-conductor thin film which should be formed, generally it is desirable that the atomic number of an impurity element to all the silicon atomic numbers in a raw material is 0.1 – 10%.

[0032] as the alkylation object of p mold impurity — BPh3, BMePh2, and B(t-Bu)3 etc. — it is mentioned. As a compound which has association with p mold impurity and Si, B(SiMe3)3, PhB(SiMe3)2, Cl2B(SiMe3), etc. are mentioned. Diboron hexahydride etc. is mentioned as a hydride of p mold impurity.

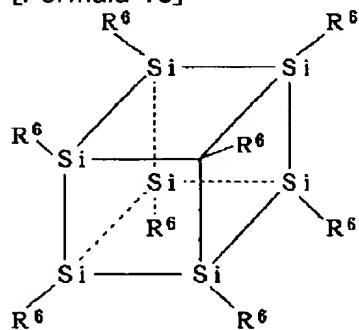
[0033] as the alkylation object of n mold impurity — PPh3, PMePh2, P(t-Bu)3, AsPh3, AsMePh2, As(t-Bu)3, SbPh3, SbMePh2, and Sb(t-Bu)3 etc. — it is mentioned. As a compound which has association with n mold impurity and Si P(SiMe3)3, PhP(SiMe3)2, Cl2P(SiMe3), As(SiMe3)3, PhAs(SiMe3)2, Cl2As(SiMe3) Sb(SiMe3)3, PhSb(SiMe3)2, Cl2Sb(SiMe3), etc. are mentioned. A phosphine, an arsine, etc. are mentioned as a hydride of n mold impurity.

[0034] When the compound which has the compound or P(As or Sb)-Si association which has especially B-Si association among the above-mentioned sources of a dopant is used, the amount of C incorporated in the semi-conductor thin film formed into these compounds since there is little association with an impurity and C can be controlled, and the electrical characteristics of a semi-conductor thin film can be improved.

[0035] In addition, when using the compound which has the compound or P(As or Sb)-Si association which has B-Si association as a source of a dopant, the OKUTASHIRA cubane expressed with the following general formula can also be used as a compound used as the source of silicon.

[0036]

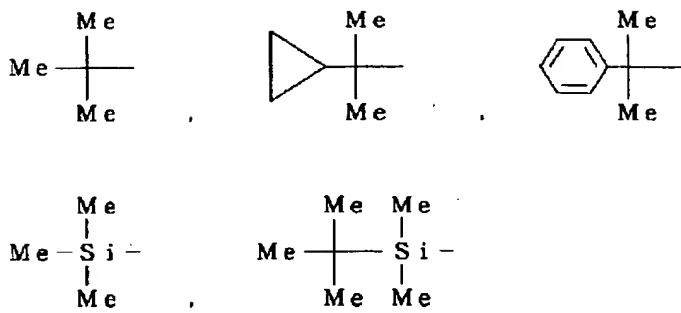
[Formula 13]



Substituent R6 A thing as shown below as an example is mentioned.

[0037]

[Formula 14]



[0038] Since the OKUTASHIRA cubane which has especially a trimethylsilyl radical (Me<sub>3</sub>Si-)  
among these substituents has the good solubility over an organic solvent, it is desirable.  
Furthermore, the solar battery of a large area can be manufactured using the formation approach  
of a semi-conductor thin film which was mentioned above in this invention. That is, since a solar  
battery has the structure which prepared the semi-conductor thin film which has one of  
conductivity types among i mold, p mold, and n mold more than two-layer in inter-electrode  
[ one pair of ], and formed semi-conductor junction, semi-conductor junction of p-n, pin, i-p, i-n,  
etc. is realizable by repeating the approach mentioned above and forming the semi-conductor  
thin film more than two-layer.

[0039] When manufacturing a solar battery by the approach of this invention, by connecting the  
two or more sets combination of a hydrogen furnace with a raw material container as shown in  
drawing 3, the laminating membrane formation of the multilayer semi-conductor thin film can be  
carried out in the consistent continuous process, and it is advantageous to manufacture of the  
solar battery of a large area.

[0040] As mentioned above, since the solution of a semi-conductor raw material is first applied  
in this invention and a semi-conductor is separated by the pyrolysis after that, even if a  
substrate is a large area, a uniform semi-conductor thin film can be formed, and the solar  
battery of a large area can be manufactured using still such an approach.

[0041] In addition, although the approach of this invention was developed by the key objective in  
manufacture of a solar battery, it is clear that it is effective also in manufacture of the  
amorphous silicon TFT of a large area. Moreover, the approach of this invention can also expect  
the application to other fields it can apply also to a substrate with a curved surface.

[0042]

[Example] Hereafter, the example of this invention is explained.

Dichlorosilane was dissolved into the example 1 tetrahydrofuran, the single dimension chain  
polysilane which adds a metal lithium, is made to carry out a polymerization on predetermined  
polymerization conditions, and is expressed with -(SiH<sub>2</sub>)<sub>n</sub>- was compounded, and it was made  
to deposit as a solid-state. n of the obtained single dimension chain polysilane was the mixture  
of the polysilane of 5-15. At a room temperature, this polysilane is a solid-state and is dissolved  
in organic solvents, such as a xylene.

[0043] The solution which dissolved this polysilane in the xylene was applied on a silicon  
substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are  
put into a hydrogen furnace, the xylene was evaporated, the pyrolysis of the polysilane was  
carried out at 650 more degrees C, and silicon was separated. Consequently, it was checked that  
the thin film of polycrystalline silicon is formed on a substrate.

[0044] Moreover, when passed hydrogen by the flow rate of 2m<sup>2</sup> / min, a pressure was set as  
1atm, UV irradiation was added with the output of 10J using a KrF excimer laser and pyrolysis  
temperature was lowered to 350 degrees C, it was checked that the thin film of an amorphous  
silicon can be formed.

[0045] Next, after the same spreading process as the above, as a result of carrying out the  
process which separates silicon by the pyrolysis in the hydrogen ambient atmosphere containing  
diboron hexahydride, it was checked that a p-type silicon thin film can be formed. Moreover,  
after the same spreading process as the above, as a result of carrying out the process which  
separates silicon by the pyrolysis in the hydrogen ambient atmosphere containing an arsine, it

was checked that n mold silicon thin film can be formed. In addition, a phosphine may be used instead of an arsine.

[0046] Furthermore, the solar battery shown in drawing 4 using the formation approach of the above silicon thin films was produced. In drawing 4, the transparent electrode 22 which consists of tin oxide (SnO<sub>2</sub>) or indium oxide tin (ITO) is formed on the glass substrate 21. On this transparent electrode 22, the laminating of p mold amorphous silicon layer 23 with a thickness of 0.1 micrometers, the undoping (i mold) amorphous silicon layer 24 with a thickness of 0.5 micrometers, and the n mold amorphous silicon layer 25 with a thickness of 0.1 micrometers is carried out one by one by repeating the process which applies and pyrolyzes a polysilane solution so that some transparent electrodes 22 may be exposed. Furthermore, on n mold amorphous silicon layer 25, the aluminum electrode 27 is formed on the transparent electrode 22 which the aluminum electrode 26 exposed, respectively.

[0047] As a result of measuring photoelectromotive force and searching for conversion efficiency about the obtained solar battery, it is 7.8% and it was checked that the conversion efficiency which is equal compared with the conventional amorphous-silicon solar cell is acquired.

[0048] The toluene of 1L was added to the reaction container filled with example 2Ar, and 2.2 mols of metals Na finely cut out in this were added. The solution which diluted the mixed liquor of one mol diethyl dichlorosilane and 0.05-mol triethyl chlorosilane with the toluene of 100mL (s) was dropped at the above-mentioned reaction container over 1 hour. Under the present circumstances, the dropping rate was controlled so that reaction temperature did not exceed 100 degrees C. It was made to react at 110 degrees C after dropping termination for further 2 hours. Then, after processing an unreacted metal by ethanol, single dimension chain polysilane was settled in ethanol. This polysilane was expressed with -(SiEt<sub>2</sub>)<sub>n</sub>-, and molecular weight was about 3000.

[0049] The solution which dissolved this polysilane in the xylene was applied on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, the xylene was evaporated, the pyrolysis of the polysilane was carried out at 450 more degrees C, and silicon was separated. Consequently, it was checked that the thin film of polycrystalline silicon is formed on a substrate.

[0050] Moreover, when passed hydrogen by the flow rate of 2m<sup>2</sup> / min, a pressure was set as 1atm, UV irradiation was added with the output of 10J using a KrF excimer laser and pyrolysis temperature was lowered to 350 degrees C, it was checked that the thin film of an amorphous silicon can be formed.

[0051] Moreover, it was checked by using the same approach as an example 1 that the silicon thin film of p mold or n mold can be formed. Furthermore, as a result of repeating these approaches, carrying out the laminating of n mold silicon thin film and the p-type silicon thin film and forming np junction, it was checked that a photoelectromotive-force property is shown.

[0052] in addition, the substituent R -CH (CH<sub>3</sub>)<sub>2</sub>, -C (CH<sub>3</sub>)<sub>3</sub>, and -C(CH<sub>3</sub>) Ph<sub>2</sub> Or -C (CH<sub>3</sub>) (cyclopropyl)<sub>2</sub> it is --- the good result was obtained also when polysilane was used.

[0053] The single dimension chain polysilane (molecular weight 5000 [ about ]) expressed with -(SiEtPh)<sub>n</sub>- as a compound used as the source of example 3 silicon was used. At a room temperature, this polysilane is a solid-state and is dissolved in organic solvents, such as a xylene.

[0054] The solution which dissolved this polysilane in the xylene was applied on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, the xylene was evaporated, the pyrolysis of the polysilane was carried out at 450 more degrees C, and silicon was separated. Consequently, it was checked that the thin film of polycrystalline silicon is formed on a substrate.

[0055] Moreover, when passed hydrogen by the flow rate of 2m<sup>2</sup> / min, a pressure was set as 1atm, UV irradiation was added with the output of 10J using a KrF excimer laser and pyrolysis temperature was lowered to 370 degrees C, it was checked that the thin film of an amorphous silicon can be formed.

[0056] Moreover, it was checked by using the same approach as an example 1 that the silicon

thin film of p mold or n mold can be formed. Furthermore, by repeating and applying the formation approach of the above silicon thin films, the multilayer silicon thin film was formed and the solar battery shown in drawing 5 was produced. In drawing 5, the molybdenum electrode 32 is formed on the stainless steel substrate 31. On this molybdenum electrode 32, sequential formation of p mold amorphous silicon layer 33 with a thickness of 0.1 micrometers, i mold amorphous silicon layer 34 with a thickness of 0.4 micrometers, and the p mold amorphous silicon layer 35 with a thickness of 0.1 micrometers is carried out. Furthermore, on p mold amorphous silicon layer 35, sequential formation of the ITO electrode 36 and the aluminum electrode 37 is carried out.

[0057] As a result of measuring photoelectromotive force and searching for conversion efficiency about the obtained solar battery, it is 8.3% and it was checked that the conversion efficiency which is equal compared with the conventional amorphous-silicon solar cell is acquired.

[0058] The annular polysilane expressed with n (n is 3 or 4) as a compound used as the source of example 4 silicon (Si<sub>2</sub>(t-Bu)) was used. At a room temperature, this annular polysilane is a solid-state and is dissolved in organic solvents, such as toluene.

[0059] The solution which dissolved this annular polysilane in toluene was applied on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, toluene was evaporated, the pyrolysis of the annular polysilane was carried out at 430 more degrees C, and silicon was separated. Consequently, it was checked that the thin film of polycrystalline silicon is formed on a substrate.

[0060] Moreover, when passed hydrogen by the flow rate of 2m<sup>2</sup> / min, a pressure was set as 1atm, UV irradiation was added with the output of 10J using a KrF excimer laser and pyrolysis temperature was lowered to 350 degrees C, it was checked that the thin film of an amorphous silicon can be formed.

[0061] Moreover, it was checked by using the same approach as an example 1 that the silicon thin film of p mold or n mold can be formed. Furthermore, by repeating and applying the formation approach of the above silicon thin films, the multilayer silicon thin film was formed and the solar battery shown in drawing 6 was produced. It sets to drawing 6 and is SiO<sub>2</sub> on the alumina substrate 41. The film 42 and Si<sub>3</sub>N<sub>4</sub> The laminating of the film 43 is carried out one by one. This Si<sub>3</sub>N<sub>4</sub> On the film 43, p mold polycrystalline silicon layer 44 of boron addition with a thickness of 10 micrometers is formed. n mold diffusion layer 45 is formed by performing Lynn diffusion in this p mold polycrystalline silicon layer 44. The ITO electrode 46 is formed on this n mold diffusion layer 45. Furthermore, the aluminum electrode 47 is formed on p mold polycrystalline silicon layer 44 exposed after mesa etching. The solar-battery property was observed also in this component.

[0062] The single dimension chain poly germane (molecular weight 3000 [ about ]) or annular poly germane who becomes a source of example 5 germanium and to whom it is expressed with -(GeEt<sub>2</sub>)<sub>n</sub> as a compound was used. At a room temperature, these compounds are solid-states and dissolve in organic solvents, such as a xylene.

[0063] The solution which dissolved these poly germane in the xylene was applied on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, the xylene was evaporated, the pyrolysis of the poly germane was carried out at 550 more degrees C, and germanium was separated. Consequently, it was checked that the thin film of polycrystal germanium is formed on a substrate.

[0064] Moreover, when passed hydrogen by the flow rate of 2m<sup>2</sup> / min, a pressure was set as 1atm, UV irradiation was added with the output of 10J using a KrF excimer laser and pyrolysis temperature was lowered to 200 degrees C, it was checked that the thin film of amorphous germanium can be formed.

[0065] The single dimension chain poly germane (molecular weight 1000 [ about ]) or annular poly germane who becomes a source of germanium and to whom it is expressed with -(GeH<sub>2</sub>)<sub>n</sub> as a compound was used using the single dimension chain polysilane (molecular weight 1000 [ about ]) or annular polysilane used as the source of example 6 silicon expressed with -(SiH<sub>2</sub>)<sub>n</sub> as a compound. At a room temperature, these compounds are solid-states and dissolve in organic

solvents, such as a xylene.

[0066] The solution which dissolved these polysilane and the poly germane in the xylene independently, respectively was applied at a mixed predetermined rate on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, the xylene was evaporated, the pyrolysis of polysilane and the poly germane was carried out at 650 more degrees C, and silicon and germanium were separated.

Consequently, it was checked that the thin film of the polycrystalline silicon-germanium corresponding to a raw material mole ratio is mostly formed on a substrate.

[0067] Moreover, when passed hydrogen by the flow rate of 2m<sup>3</sup> / min, a pressure was set as 1atm, UV irradiation was added with the output of 10J using a KrF excimer laser and pyrolysis temperature was lowered to 350 degrees C, it was checked that the thin film of amorphous silicon-germanium can be formed.

[0068] As a result of carrying out the laminating of Si thin film and the SiGe mixing thin film combining the above approaches, adding a donor and an acceptor in each layer and forming np junction, it became clear that a solar-battery property is shown.

[0069] It is P(SiMe<sub>3</sub>)<sub>3</sub> as a compound used as the single dimension chain polysilane (molecular weight 12000 [ about ]) expressed with -(SiHPh) n- as a compound used as the source of example 7 silicon, and the source of n mold impurity. It used. After carrying out the spin coat of the toluene solution of the mixture of these compounds on a quartz substrate, the vacuum drying was carried out at 70 degrees C for 1 hour. Subsequently, to the bottom of the mixed air current of an argon and hydrogen, it heated at 700 degrees C by 300 degrees C for 1 hour for 1 hour, and the pyrolysis of the raw material was carried out. Consequently, the silicon thin film with which Lynn was doped was formed.

[0070] Si<sub>5</sub> Cl<sub>12</sub> which is one sort of the compound called par chlorosilicane as a halogenide used as the source of example 8 silicon was used. The melting point is 345 degrees C and this compound dissolves in organic solvents, such as the petroleum ether.

[0071] The solution which dissolved this Si<sub>5</sub> Cl<sub>12</sub> in the petroleum ether was applied on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, the petroleum ether was evaporated, the pyrolysis of Si<sub>5</sub> Cl<sub>12</sub> was carried out at 450 more degrees C, and silicon was separated. Consequently, it was checked that the thin film of an amorphous silicon is formed on a substrate. Moreover, it was checked by raising heating temperature that the thin film of polycrystalline silicon can be formed.

[0072] Next, after the same spreading process as the above, as a result of carrying out the process which separates silicon by the pyrolysis in the hydrogen ambient atmosphere containing diboron hexahydride, it was checked that a p-type silicon thin film can be formed. Moreover, after the same spreading process as the above, as a result of carrying out the process which separates silicon by the pyrolysis in the hydrogen ambient atmosphere containing an arsine, it was checked that n mold silicon thin film can be formed. In addition, a phosphine may be used instead of an arsine.

[0073] Furthermore, the solar battery shown in drawing 4 using the formation approach of the above silicon thin films was produced. As a result of measuring photoelectromotive force and searching for conversion efficiency about the obtained solar battery, it is 8.5% and it was checked that the conversion efficiency which is equal compared with the conventional amorphous-silicon solar cell is acquired.

[0074] Si<sub>6</sub> Cl<sub>14</sub> was used as a halogenide used as the source of example 9 silicon. The melting point is 320 degrees C and this compound dissolves in organic solvents, such as the petroleum ether.

[0075] The solution which dissolved this Si<sub>6</sub> Cl<sub>14</sub> in the petroleum ether was applied on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, the petroleum ether was evaporated, the pyrolysis of Si<sub>6</sub> Cl<sub>14</sub> was carried out at 440 more degrees C, and silicon was separated. Consequently, it was checked that the thin film of an amorphous silicon is formed on a substrate. Moreover, it was checked by raising heating temperature that the thin film of polycrystalline silicon can be formed.

[0076] Moreover, it was checked by using the same approach as an example 8 that the silicon

thin film of p mold or n mold can be formed. Furthermore, as a result of repeating these approaches, carrying out the laminating of n mold silicon thin film and the p-type silicon thin film and forming np junction, it was checked that a photoelectromotive-force property is shown.

[0077] Same Si<sub>5</sub> Cl<sub>12</sub> as having used in the example 8 as a halogenide used as the source of example 10 silicon was used. This Si<sub>5</sub> Cl<sub>12</sub> was applied by mechanical actuation at the temperature near the melting point on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, the petroleum ether was evaporated, the pyrolysis of Si<sub>5</sub> Cl<sub>12</sub> was carried out at 450 more degrees C, and silicon was separated. Consequently, it was checked that the thin film of an amorphous silicon is formed on a substrate. Moreover, it was checked by raising heating temperature that the thin film of polycrystalline silicon can be formed.

[0078] Moreover, it was checked by using the same approach as an example 8 that the silicon thin film of p mold or n mold can be formed. Furthermore, by repeating and applying the formation approach of the above silicon thin films, the multilayer silicon thin film was formed and the solar battery shown in drawing 5 was produced. As a result of measuring photoelectromotive force and searching for conversion efficiency about the obtained solar battery, it is 14% and it was checked that the conversion efficiency which is equal compared with the conventional amorphous-silicon solar cell is acquired.

[0079] Same Si<sub>6</sub> Cl<sub>14</sub> as having used in the example 9 as a halogenide used as the source of example 11 silicon was used. This Si<sub>6</sub> Cl<sub>14</sub> was applied by mechanical actuation at the temperature near the melting point on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, the petroleum ether was evaporated, the pyrolysis of Si<sub>6</sub> Cl<sub>14</sub> was carried out at 440 more degrees C, and silicon was separated. Consequently, it was checked that the thin film of an amorphous silicon is formed on a substrate. Moreover, it was checked by raising heating temperature that the thin film of polycrystalline silicon can be formed.

[0080] Moreover, it was checked by using the same approach as an example 8 that the silicon thin film of p mold or n mold can be formed. Furthermore, by repeating and applying the formation approach of the above silicon thin films, the multilayer silicon thin film was formed and the solar battery shown in drawing 6 was produced. The solar-battery property was observed also in this component.

[0081] germanium<sub>5</sub> Cl<sub>12</sub> was used as a halogenide used as the source of example 12 germanium. This compound dissolves in organic solvents, such as the petroleum ether. The solution which dissolved this germanium<sub>5</sub> Cl<sub>12</sub> in the petroleum ether was applied on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, the petroleum ether was evaporated, the pyrolysis of germanium<sub>5</sub> Cl<sub>12</sub> was carried out at 400 more degrees C, and germanium was separated. Consequently, it was checked that the thin film of polycrystal germanium is formed on a substrate. Moreover, when UV irradiation was added and pyrolysis temperature was lowered, it was checked that the thin film of amorphous germanium can be formed.

[0082] Si<sub>5</sub> Br<sub>12</sub> was used as a halogenide used as the source of example 13 silicon. This Si<sub>5</sub> Br<sub>12</sub> was applied by mechanical actuation at the temperature near the melting point on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, the petroleum ether was evaporated, the pyrolysis of Si<sub>5</sub> Br<sub>12</sub> was carried out at 440 more degrees C, and silicon was separated. Consequently, it was checked that the thin film of an amorphous silicon is formed on a substrate. Moreover, it was checked by raising heating temperature that the thin film of polycrystalline silicon can be formed.

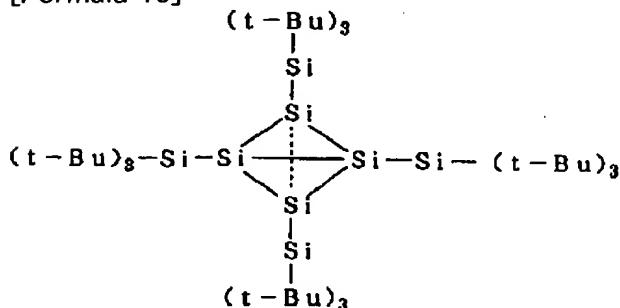
[0083] Moreover, it was checked by using the same approach as an example 8 that the silicon thin film of p mold or n mold can be formed. Furthermore, by repeating and applying the formation approach of the above silicon thin films, the multilayer silicon thin film was formed and the solar battery shown in drawing 6 was produced. The solar-battery property was observed also in this component.

[0084] The solution which dissolved in the xylene the silane system compound shown with the following chemical formula as a source of example 14 silicon was applied on a silicon substrate, a

quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, the xylene was evaporated, the pyrolysis of the silane system compound was carried out at 650 more degrees C, and silicon was separated. Consequently, it was checked that the thin film of polycrystalline silicon is formed on a substrate.

[0085]

[Formula 15]



[0086] Moreover, when passed hydrogen by the flow rate of 2m<sup>2</sup> / min, a pressure was set as 1atm, UV irradiation was added with the output of 10J using a KrF excimer laser and pyrolysis temperature was lowered to 350 degrees C, it was checked that the thin film of an amorphous silicon can be formed.

[0087] Next, after the same spreading process as the above, as a result of carrying out the process which separates silicon by the pyrolysis in the hydrogen ambient atmosphere containing diboron hexahydride, it was checked that a p-type silicon thin film can be formed. Moreover, after the same spreading process as the above, as a result of carrying out the process which separates silicon by the pyrolysis in the hydrogen ambient atmosphere containing an arsine, it was checked that n mold silicon thin film can be formed. In addition, a phosphine may be used instead of an arsine.

[0088] Furthermore, the solar battery shown in drawing 4 using the formation approach of the above silicon thin films was produced. As a result of measuring photoelectromotive force and searching for conversion efficiency about the obtained solar battery, it is 8.5% and it was checked that the conversion efficiency which is equal compared with the conventional amorphous-silicon solar cell is acquired.

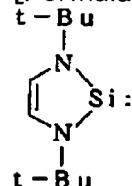
[0089] Similarly, the solar battery shown in drawing 5 was produced. As a result of measuring photoelectromotive force and searching for conversion efficiency about the obtained solar battery, it is 8.3% and it was checked that the conversion efficiency which is equal compared with the conventional amorphous-silicon solar cell is acquired.

[0090] Similarly, the solar battery shown in drawing 6 was produced. The solar-battery property was observed also in this component.

It is P(SiMe<sub>3</sub>)<sub>3</sub> as the silylene system compound shown with the following chemical formula as a compound used as the source of example 15 silicon, and a compound used as the source of n mold impurity. It used. After carrying out the spin coat of the toluene solution of the mixture of these compounds on a quartz substrate, the vacuum drying was carried out at 70 degrees C for 1 hour. Subsequently, to the bottom of the mixed air current of an argon and hydrogen, it heated at 600 degrees C by 300 degrees C for 1 hour for 1 hour, and the pyrolysis of the raw material was carried out. Consequently, the silicon thin film with which Lynn was doped was formed.

[0091]

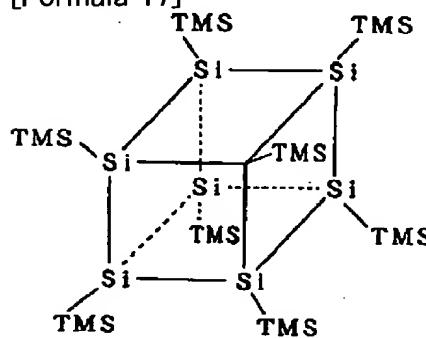
[Formula 16]



[0092] It is P(SiMe<sub>3</sub>)<sub>3</sub> as the OKUTASHIRA cubane compound which has the trimethylsilyl radical (TMS) shown with the following chemical formula as a compound used as the source of example 16 silicon, and a compound used as the source of n mold impurity. It used. After carrying out the spin coat of the toluene solution of the mixture of these compounds on a quartz substrate, the vacuum drying was carried out at 70 degrees C for 1 hour. Subsequently, to the bottom of the mixed air current of an argon and hydrogen, it heated at 600 degrees C by 300 degrees C for 1 hour for 1 hour, and the pyrolysis of the raw material was carried out. Consequently, the silicon thin film with which Lynn was doped was formed.

[0093]

[Formula 17]



[0094]

[Effect of the Invention] If the approach of this invention is used as explained in full detail above, by adopting two processes of spreading and the pyrolysis of the solution of a semi-conductor raw material, the semi-conductor thin film which consists of the silicon or germanium of a large area can be formed easily, and the solar battery of a large area can be further manufactured using this approach.

---

[Translation done.]

**\* NOTICES \***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**TECHNICAL FIELD**

---

**[Field of the Invention]** This invention relates to the manufacture approach of a solar battery of having used the new semi-conductor thin film formation approach and this approach.

---

[Translation done.]

**\* NOTICES \***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**PRIOR ART**

[Description of the Prior Art] Conventionally, as an approach of forming the semi-conductor thin film which consists of the silicon or germanium which is IV group element, vapor growth, such as vacuum deposition, a spatter, the ion plating method, and a CVD method, is used. However, in order that each of these approaches might use a reduced pressure environment, a hydrogen furnace environment, etc. at the time of membrane formation, it was indispensable to have used an airtight high reaction container, and they was difficult to form a uniform semi-conductor thin film on the substrate of a large area. For this reason, there was a limitation in manufacturing what has a single or more large figures area by the conventional ratio with the application product which has a semi-conductor thin film, for example, a solar battery.

[0003] Then, it considers using the wet applying method as one of the approaches of forming the semi-conductor thin film of a large area. For example, the approach of forming a silicon thin film is indicated by JP,4-119996,A by applying compounds, such as OKUTASHIRA cubane, as a source of silicon on a substrate, and pyrolyzing this source compound of silicon. This approach does not need a large-scale and expensive manufacturing facility like a vacuum chamber, but it is thought that it is advantageous to forming a silicon thin film easily on the substrate of a large area.

[0004] However, to oxygen, compounds, such as OKUTASHIRA cubane indicated by this official report, have many unstable things, in air, oxidize easily and denaturalize. Moreover, these compounds have that the solubility to a solvent is [ much ] low, and are difficult to form a uniform thin film.

[0005] Furthermore, if the application to a solar battery etc. is taken into consideration, it is necessary to form the silicon thin film which doped the impurity of p mold or n mold. However, conventionally, since the impurity was doped by thermal diffusion or the ion implantation after forming a silicon thin film by the pyrolysis, large-scale equipment was needed and complication of a process had been caused.

---

[Translation done.]

**\* NOTICES \***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**EFFECT OF THE INVENTION**

---

[Effect of the Invention] If the approach of this invention is used as explained in full detail above, by adopting two processes of spreading and the pyrolysis of the solution of a semi-conductor raw material, the semi-conductor thin film which consists of the silicon or germanium of a large area can be formed easily, and the solar battery of a large area can be further manufactured using this approach.

---

[Translation done.]

**\* NOTICES \***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**TECHNICAL PROBLEM**

---

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the approach of forming easily the semi-conductor thin film which consists of the silicon or germanium of a large area, and the method of manufacturing the solar battery of a large area using this approach.

---

[Translation done.]

## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

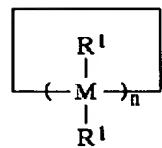
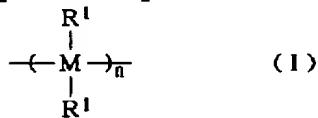
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## MEANS

[Means for Solving the Problem] General formula (I) After the semi-conductor thin film formation approach of this invention applies the solution of a semi-conductor raw material on a substrate, it is the approach of pyrolyzing, separating a semi-conductor and forming a semi-conductor thin film, and said semi-conductor raw material reaches (II).

[0008]

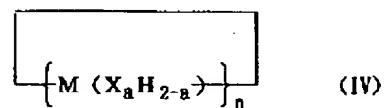
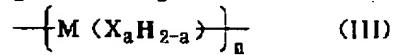
[Formula 6]



(— M is chosen from the group which consists of silicon and germanium among a formula, and R1 is independently chosen from the group which consists of hydrogen, a with a carbon numbers of two or more in which at least beta has hydrogen alkyl group and a phenyl group, and a silyl radical, respectively. ) — the compound and general formula (III) which are expressed — and (IV)

[0009]

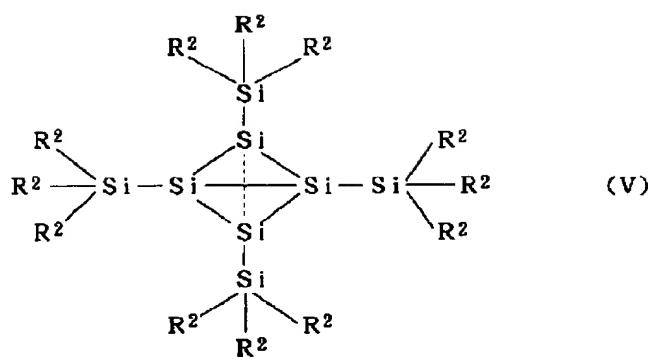
[Formula 7]



(— M is chosen from the group which consists of silicon and germanium among a formula, and X is [ four or more integers and a of a halogen atom and n ] 1 or 2.) — the compound and general formula (V) which are expressed

[0010]

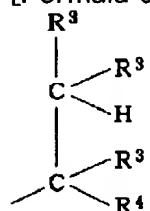
[Formula 8]



(R2 is independently chosen from the group which consists of the permutation expressed with the following type or an unsubstituted alkyl group, an aryl group, and an aralkyl radical among a formula, respectively.)

[0011]

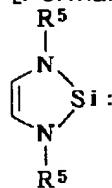
[Formula 9]



the inside of a formula, and R3 — respectively — independent — the permutation of a hydrogen atom and carbon numbers 1–15, or an unsubstituted alkyl group — It is chosen from the group which consists of the permutation or unsubstituted aralkyl radical of the permutation of carbon numbers 6–15 or an unsubstituted aryl group, and carbon numbers 7–15. R4 It is chosen from the group which consists of the permutation or unsubstituted aralkyl radical of the permutation of the permutation of carbon numbers 1–15 or an unsubstituted alkyl group, and carbon numbers 6–15 or an unsubstituted aryl group, and carbon numbers 7–15. The compound expressed and a general formula (VI)

[0012]

[Formula 10]



(— R5 is independently chosen from the group which consists of a permutation or an unsubstituted silyl radical with the permutation of carbon numbers 1–15 or an unsubstituted alkyl group, an aryl group, an aralkyl radical, and 1–5 silicon among a formula, respectively.) — it is chosen from the group which consists of a compound expressed.

[0013] After the formation approach of a semi-conductor thin film in this invention of having a predetermined conductivity type adds the source of a dopant which gives the conductivity type of p mold or n mold to the solution of the semi-conductor raw material chosen from the group which consists of a compound expressed with said general formula (I) – (VI) and applies it on a substrate, it separates the semi-conductor which pyrolyzes and contains the impurity of a predetermined conductivity type.

[0014] Other formation approaches of a semi-conductor thin film in this invention of having a predetermined conductivity type separate the semi-conductor which pyrolyzes in the ambient atmosphere containing the source of a dopant which gives the conductivity type of p mold or n mold, and contains the impurity of a predetermined conductivity type, after applying on a

substrate the solution of the semi-conductor raw material chosen from the group which consists of a compound expressed with said general formula (I) – (VI).

[0015] In the manufacture approach of the solar battery of this invention manufacturing the solar battery which prepared the semi-conductor thin film which has one of conductivity types among i mold, p mold, and n mold more than two-layer in inter-electrode [ one pair of ], and formed semi-conductor junction in it In forming the semi-conductor thin film of i mold, after applying on a substrate the solution of the semi-conductor raw material chosen from the group which consists of a compound expressed with said general formula (I) – (VI), In adopting the process which it pyrolyzes [ process ] and separates a semi-conductor and forming the semi-conductor thin film of p mold or n mold Said general formula (I) [ whether it pyrolyzes, after adding the source of a dopant which gives a predetermined conductivity type to the solution of the semi-conductor raw material chosen from the group which consists of a compound expressed with – (VI) and applying on a substrate, and ] Or by pyrolyzing in the ambient atmosphere containing the source of a dopant which gives a predetermined conductivity type after applying on a substrate the solution of the semi-conductor raw material chosen from the group which consists of a compound expressed with said general formula (I) – (VI) The process which separates the semi-conductor containing the impurity which gives a predetermined conductivity type is adopted, these processes are repeated, and the semi-conductor thin film more than two-layer is formed.

[0016]

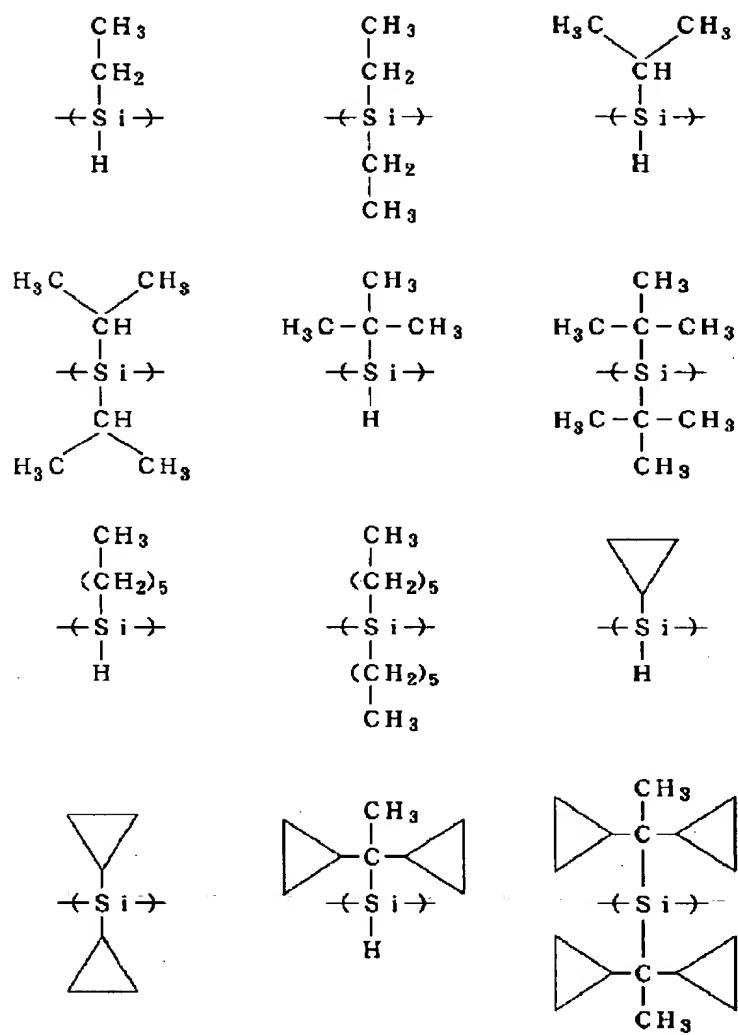
[Embodiment of the Invention] Hereafter, this invention is further explained to a detail. In this invention, the ingredient of the arbitration chosen from semi-conductors, such as silicon, glass, the glass that has a transparent electrode, a metal, the ceramics, a thermally stable polymer, etc. as a substrate ingredient can be used.

[0017] The compound used as the semi-conductor raw material used in this invention is explained. The compound expressed with a general formula (I) or (II) is the silane system which makes a single dimension chain or cyclic structure, or a germane system compound. A copolymer is sufficient as these compounds and they may be used as mixture. In this invention, it is a solid-state at a room temperature, and a meltable compound is used for an organic solvent. In order to fulfill such conditions, it is desirable that polymerization degree n is 10000 or less [ 3 or more ] in the polymer which has for example, single dimension chain structure, and it is more desirable to a pan that it is 5–30.

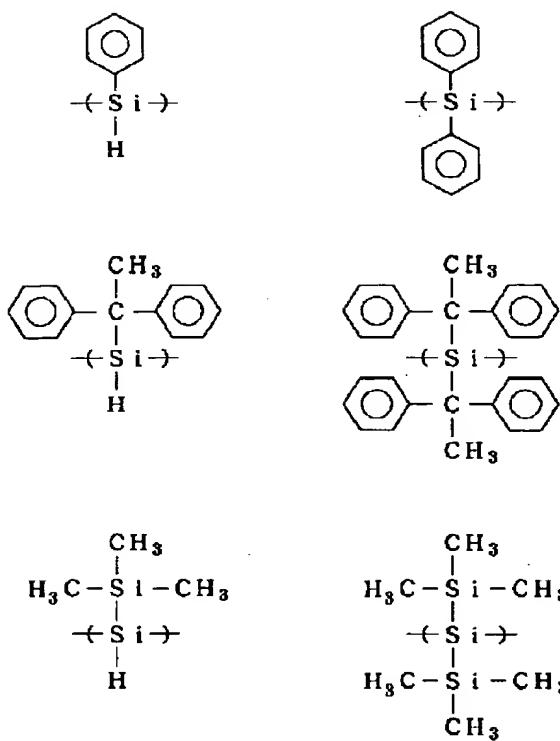
[0018] The example of a compound expressed with a general formula (I) or (II) is shown below. In addition, although only the polysilane of a single dimension chain is shown below, annular polysilane is sufficient and, of course, the poly germane who transposed silicon to germanium is sufficient.

[0019]

[Formula 11]



[0020]  
 [Formula 12]



[0021] The compound expressed with a general formula (III) or (IV) is a halogenide of silicon or/and germanium. In order to fulfill the conditions of being meltable, to an organic solvent, as for these halogenides, it is desirable that weight average molecular weight is 500–100,000. Since it volatilizes from a substrate before a pyrolysis will happen, if molecular weight is small, the good film is hard to be formed. If molecular weight is the above-mentioned range, the vapor pressure in pyrolysis temperature is comparatively low, and the volatilization from a substrate can be disregarded. If molecular weight is too large, the solubility over a solvent will fall and spreading to a substrate will become difficult.

[0022] It is a solid-state at a room temperature, and the silane system compound expressed with a general formula (V) is meltable to an organic solvent, and its stability over oxidation is high. It is a solid-state at a room temperature, and the silylene compound expressed with a general formula (VI) is meltable to an organic solvent, and its stability over oxidation is high.

[0023] Since the compound expressed with general formula (I) – (VI) used in this invention is meltable to an organic solvent, it is applied on the substrate which has the flat surface or curved surface of a large area by the method of applying arbitration, such as dipping, spin coating, and spray coating, and can form a uniform paint film. As for the thickness of a paint film, it is desirable that it is dozens of nm. The instrument used at this spreading process can be chosen as arbitration according to the magnitude of a substrate. Moreover, if atmospheric mixing can be prevented about a coater, it is enough and a large-scale airtight high decompression device like [ in the case of vapor growth ] is unnecessary.

[0024] In this invention, after heating the paint film of the compound applied on the substrate before and behind the melting point in reducing atmospheres, such as a predetermined ambient atmosphere, for example, an inert gas ambient atmosphere, or hydrogen, and evaporating a solvent, by making a pyrolysis reaction cause, silicon or/and germanium are separated and a semi-conductor thin film is formed. The pressure of an ambient atmosphere is good before and behind ordinary pressure (one atmospheric pressure). Moreover, as for a resultant, removing with exhaust air is desirable. Especially a heating means may not be limited, but may use a common electric furnace, may irradiate infrared radiation like the rapid thermal annealing method, and may perform laser annealing. Concrete pyrolysis temperature changes with compounds. For example, in the case of the compound expressed with a general formula (I) and (II), it is desirable to carry out a pyrolysis at 200–700 degrees C and further 300–650 degrees C. In the case of the

compound expressed with a general formula (III) and (IV), a pyrolysis happens in about 250 degrees C – about 1300 degrees C, but it is desirable to carry out a pyrolysis at 300–500 degrees C. In the case of the compound expressed with a general formula (V) and (VI), it is desirable to carry out a pyrolysis at 300–700 degrees C. A programming rate is set as 5 degrees C / min extent. Reaction time is enough in 10 minutes – 10 hours. However, a temperature up may not be carried out depending on the case, but the pyrolysis in constant temperature may be performed.

[0025] By this pyrolysis reaction, the elimination reaction of the substituent introduced into the side chain of a semi-conductor raw material occurs. For example, a beta elimination reaction occurs with the compound which has a with a carbon numbers of two or more in which at least beta has hydrogen alkyl group, and radical desorption happens with the compound which has a phenyl group. Silicon or the polycrystal thin film of germanium can be formed by such pyrolysis reaction. Moreover, decomposition by UV irradiation is used together, and if pyrolysis temperature is reduced, an amorphous thin film can be formed. In addition, these thin films contain some hydrogen in addition to IV group element.

[0026] The mixed semi-conductor thin film of silicon and germanium can also be formed by applying and carrying out the pyrolysis of the solution of the mixture of a silane system compound and a germane system compound, or the solution of the copolymer which has the repeat unit of a silane, and germane's repeat unit. In addition, for controlling a presentation with silicon and germanium, the former approach is more desirable.

[0027] The equipment for enforcing the approach of above this inventions is typically shown in drawing 1 – drawing 3. As shown in drawing 1 (a), in order to put in a substrate 1 in the coater 3 equipped with the nozzle 4 and to prevent atmospheric-air mixing into a coater 3, after considering as nitrogen-gas-atmosphere mind, the solution of a semi-conductor raw material is sprayed from a nozzle 4, and it applies on a substrate 1. In this case, the amount of the solution applied on a substrate 1 is controllable by setting up nozzle dimensions and spraying time amount suitably. Next, as shown in drawing 1 (b), the substrate 1 with which the solution of a semi-conductor raw material was applied is put into the hydrogen furnace 5, a substrate 1 is heated at a heater 6 in the reducibility gas ambient atmosphere which makes hydrogen a subject, the pyrolysis of the semi-conductor raw material is carried out, and the semi-conductor thin film 2 is formed on a substrate 1. In addition, an infrared heater, a resistance heating heater, etc. can be used as a heater 6.

[0028] As shown in drawing 2, a substrate 1 is put in in the hydrogen furnace 5, and the solution of a semi-conductor raw material can be directly sprayed from a nozzle 4 on a substrate 1, it can apply on a substrate 1, a substrate 1 can be heated at a heater 6, and a semi-conductor thin film can also be formed by pyrolyzing a semi-conductor raw material.

[0029] Moreover, drawing 3 shows the equipment for manufacturing a semi-conductor thin film continuously using a flexible substrate. The flexible substrate 1 is supplied from a supply roll 11, and it is immersed in the semi-conductor raw material solution 8 in the raw material container 7. A substrate 1 is sent to the hydrogen furnace 5 with the delivery rolls 12 and 12. It is heated at a heater 6 in the hydrogen furnace 5, the pyrolysis of a semi-conductor raw material is performed, and a semi-conductor thin film is formed on a substrate 1. Then, a substrate 1 is rolled round and rolled round by the roll 13. Thus, a semi-conductor thin film can be continuously formed on a flexible substrate.

[0030] In this invention, the semi-conductor thin film of a predetermined conductivity type can also be formed by using the source of a dopant which gives the conductivity type of p mold or n mold. The two following approaches can be used as the approach. Namely, after adding the source of a dopant which gives the conductivity type of p mold or n mold to the solution of the semi-conductor raw material chosen from the group which consists of a compound expressed with (1) general-formula (I) – (VI) and applying on a substrate, How to separate the semi-conductor which pyrolyzes and contains the impurity of a predetermined conductivity type, And after applying on a substrate the solution of the semi-conductor raw material chosen from the group which consists of a compound expressed with (2) general-formula (I) – (VI), It is the approach of separating the semi-conductor which pyrolyzes in the ambient atmosphere

containing the source of a dopant which gives the conductivity type of p mold or n mold, and contains the impurity of a predetermined conductivity type. The equipment and the reaction condition for enforcing these approaches are the same with having indicated previously, and good.

[0031] In these approaches, generally, boron (B) is used as a p mold impurity, and Lynn (P), an arsenic (As), and antimony (Sb) are used as an n mold impurity. By the approach of (1), the alkylation object of an impurity element or the compound which has association with an impurity element and Si in intramolecular is used as a source of a dopant. By the approach of (2), the alkylation object of an impurity element, the compound which has association with an impurity element and Si in intramolecular, or the hydride of an impurity element is used as a source of a dopant. Although the addition of the source of a dopant to a semi-conductor raw material is based on high impurity concentration required for the semi-conductor thin film which should be formed, generally it is desirable that the atomic number of an impurity element to all the silicon atomic numbers in a raw material is 0.1 – 10%.

[0032] as the alkylation object of p mold impurity — BPh3, BMePh2, and B(t-Bu)3 etc. — it is mentioned. As a compound which has association with p mold impurity and Si, B(SiMe3)3, PhB(SiMe3)2, Cl2 B(SiMe3), etc. are mentioned. Diboron hexahydride etc. is mentioned as a hydride of p mold impurity.

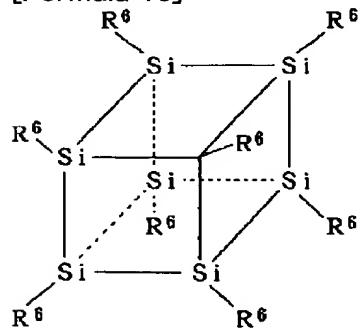
[0033] as the alkylation object of n mold impurity — PPh3, PMePh2, P(t-Bu)3, AsPh3, AsMePh2, As(t-Bu)3, SbPh3, SbMePh2, and Sb(t-Bu)3 etc. — it is mentioned. As a compound which has association with n mold impurity and Si P(SiMe3)3, PhP(SiMe3)2, Cl2 P(SiMe3), As(SiMe3)3, PhAs(SiMe3)2, Cl2 As(SiMe3) Sb(SiMe3)3, PhSb(SiMe3)2, Cl2 Sb(SiMe3), etc. are mentioned. A phosphine, an arsine, etc. are mentioned as a hydride of n mold impurity.

[0034] When the compound which has the compound or P(As or Sb)-Si association which has especially B-Si association among the above-mentioned sources of a dopant is used, the amount of C incorporated in the semi-conductor thin film formed into these compounds since there is little association with an impurity and C can be controlled, and the electrical characteristics of a semi-conductor thin film can be improved.

[0035] In addition, when using the compound which has the compound or P(As or Sb)-Si association which has B-Si association as a source of a dopant, the OKUTASHIRA cubane expressed with the following general formula can also be used as a compound used as the source of silicon.

[0036]

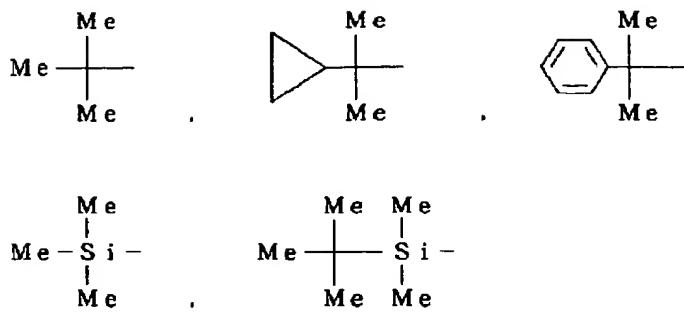
[Formula 13]



Substituent R6 A thing as shown below as an example is mentioned.

[0037]

[Formula 14]



[0038] Since the OKUTASHIRA cubane which has especially a trimethylsilyl radical (Me<sub>3</sub>Si-) among these substituents has the good solubility over an organic solvent, it is desirable. Furthermore, the solar battery of a large area can be manufactured using the formation approach of a semi-conductor thin film which was mentioned above in this invention. That is, since a solar battery has the structure which prepared the semi-conductor thin film which has one of conductivity types among i mold, p mold, and n mold more than two-layer in inter-electrode [ one pair of ], and formed semi-conductor junction, semi-conductor junction of p-n, pin, i-p, i-n, etc. is realizable by repeating the approach mentioned above and forming the semi-conductor thin film more than two-layer.

[0039] When manufacturing a solar battery by the approach of this invention, by connecting the two or more sets combination of a hydrogen furnace with a raw material container as shown in drawing 3, the laminating membrane formation of the multilayer semi-conductor thin film can be carried out in the consistent continuous process, and it is advantageous to manufacture of the solar battery of a large area.

[0040] As mentioned above, since the solution of a semi-conductor raw material is first applied in this invention and a semi-conductor is separated by the pyrolysis after that, even if a substrate is a large area, a uniform semi-conductor thin film can be formed, and the solar battery of a large area can be manufactured using still such an approach.

[0041] In addition, although the approach of this invention was developed by the key objective in manufacture of a solar battery, it is clear that it is effective also in manufacture of the amorphous silicon TFT of a large area. Moreover, the approach of this invention can also expect the application to other fields it can apply also to a substrate with a curved surface.

---

[Translation done.]

## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## EXAMPLE

[Example] Hereafter, the example of this invention is explained.

Dichlorosilane was dissolved into the example 1 tetrahydrofuran, the single dimension chain polysilane which adds a metal lithium, is made to carry out a polymerization on predetermined polymerization conditions, and is expressed with  $-(SiH_2)_n-$  was compounded, and it was made to deposit as a solid-state.  $n$  of the obtained single dimension chain polysilane was the mixture of the polysilane of 5-15. At a room temperature, this polysilane is a solid-state and is dissolved in organic solvents, such as a xylene.

[0043] The solution which dissolved this polysilane in the xylene was applied on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, the xylene was evaporated, the pyrolysis of the polysilane was carried out at 650 more degrees C, and silicon was separated. Consequently, it was checked that the thin film of polycrystalline silicon is formed on a substrate.

[0044] Moreover, when passed hydrogen by the flow rate of 2m<sup>3</sup> / min, a pressure was set as 1atm, UV irradiation was added with the output of 10J using a KrF excimer laser and pyrolysis temperature was lowered to 350 degrees C, it was checked that the thin film of an amorphous silicon can be formed.

[0045] Next, after the same spreading process as the above, as a result of carrying out the process which separates silicon by the pyrolysis in the hydrogen ambient atmosphere containing diboron hexahydride, it was checked that a p-type silicon thin film can be formed. Moreover, after the same spreading process as the above, as a result of carrying out the process which separates silicon by the pyrolysis in the hydrogen ambient atmosphere containing an arsine, it was checked that n mold silicon thin film can be formed. In addition, a phosphine may be used instead of an arsine.

[0046] Furthermore, the solar battery shown in drawing 4 using the formation approach of the above silicon thin films was produced. In drawing 4, the transparent electrode 22 which consists of tin oxide (SnO<sub>2</sub>) or indium oxide tin (ITO) is formed on the glass substrate 21. On this transparent electrode 22, the laminating of p mold amorphous silicon layer 23 with a thickness of 0.1 micrometers, the undoping (i mold) amorphous silicon layer 24 with a thickness of 0.5 micrometers, and the n mold amorphous silicon layer 25 with a thickness of 0.1 micrometers is carried out one by one by repeating the process which applies and pyrolyzes a polysilane solution so that some transparent electrodes 22 may be exposed. Furthermore, on n mold amorphous silicon layer 25, the aluminum electrode 27 is formed on the transparent electrode 22 which the aluminum electrode 26 exposed, respectively.

[0047] As a result of measuring photoelectromotive force and searching for conversion efficiency about the obtained solar battery, it is 7.8% and it was checked that the conversion efficiency which is equal compared with the conventional amorphous-silicon solar cell is acquired.

[0048] The toluene of 1L was added to the reaction container filled with example 2Ar, and 2.2 mols of metals Na finely cut out in this were added. The solution which diluted the mixed liquor of one mol diethyl dichlorosilane and 0.05-mol triethyl chlorosilicane with the toluene of 100mL (s) was dropped at the above-mentioned reaction container over 1 hour. Under the present

circumstances, the dropping rate was controlled so that reaction temperature did not exceed 100 degrees C. It was made to react at 110 degrees C after dropping termination for further 2 hours. Then, after processing an unreacted metal by ethanol, single dimension chain polysilane was settled in ethanol. This polysilane was expressed with -(SiEt<sub>2</sub>)<sub>n</sub>-, and molecular weight was about 3000.

[0049] The solution which dissolved this polysilane in the xylene was applied on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, the xylene was evaporated, the pyrolysis of the polysilane was carried out at 450 more degrees C, and silicon was separated. Consequently, it was checked that the thin film of polycrystalline silicon is formed on a substrate.

[0050] Moreover, when passed hydrogen by the flow rate of 2m<sup>2</sup> / min, a pressure was set as 1atm, UV irradiation was added with the output of 10J using a KrF excimer laser and pyrolysis temperature was lowered to 350 degrees C, it was checked that the thin film of an amorphous silicon can be formed.

[0051] Moreover, it was checked by using the same approach as an example 1 that the silicon thin film of p mold or n mold can be formed. Furthermore, as a result of repeating these approaches, carrying out the laminating of n mold silicon thin film and the p-type silicon thin film and forming np junction, it was checked that a photoelectromotive-force property is shown.

[0052] in addition, the substituent R -CH (CH<sub>3</sub>)<sub>2</sub>, -C (CH<sub>3</sub>)<sub>3</sub>, and -C(CH<sub>3</sub>) Ph<sub>2</sub> Or -C (CH<sub>3</sub>) (cyclopropyl)<sub>2</sub> it is — the good result was obtained also when polysilane was used.

[0053] The single dimension chain polysilane (molecular weight 5000 [ about ]) expressed with -(SiEtPh)<sub>n</sub>- as a compound used as the source of example 3 silicon was used. At a room temperature, this polysilane is a solid-state and is dissolved in organic solvents, such as a xylene.

[0054] The solution which dissolved this polysilane in the xylene was applied on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, the xylene was evaporated, the pyrolysis of the polysilane was carried out at 450 more degrees C, and silicon was separated. Consequently, it was checked that the thin film of polycrystalline silicon is formed on a substrate.

[0055] Moreover, when passed hydrogen by the flow rate of 2m<sup>2</sup> / min, a pressure was set as 1atm, UV irradiation was added with the output of 10J using a KrF excimer laser and pyrolysis temperature was lowered to 370 degrees C, it was checked that the thin film of an amorphous silicon can be formed.

[0056] Moreover, it was checked by using the same approach as an example 1 that the silicon thin film of p mold or n mold can be formed. Furthermore, by repeating and applying the formation approach of the above silicon thin films, the multilayer silicon thin film was formed and the solar battery shown in drawing 5 was produced. In drawing 5 , the molybdenum electrode 32 is formed on the stainless steel substrate 31. On this molybdenum electrode 32, sequential formation of p mold amorphous silicon layer 33 with a thickness of 0.1 micrometers, i mold amorphous silicon layer 34 with a thickness of 0.4 micrometers, and the p mold amorphous silicon layer 35 with a thickness of 0.1 micrometers is carried out. Furthermore, on p mold amorphous silicon layer 35, sequential formation of the ITO electrode 36 and the aluminum electrode 37 is carried out.

[0057] As a result of measuring photoelectromotive force and searching for conversion efficiency about the obtained solar battery, it is 8.3% and it was checked that the conversion efficiency which is equal compared with the conventional amorphous-silicon solar cell is acquired.

[0058] The annular polysilane expressed with n (n is 3 or 4) as a compound used as the source of example 4 silicon (Si<sub>2</sub> (t-Bu)) was used. At a room temperature, this annular polysilane is a solid-state and is dissolved in organic solvents, such as toluene.

[0059] The solution which dissolved this annular polysilane in toluene was applied on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, toluene was evaporated, the pyrolysis of the annular polysilane was carried out at 430 more degrees C, and silicon was separated. Consequently, it was checked that

the thin film of polycrystalline silicon is formed on a substrate.

[0060] Moreover, when passed hydrogen by the flow rate of 2m<sup>2</sup> / min, a pressure was set as 1atm, UV irradiation was added with the output of 10J using a KrF excimer laser and pyrolysis temperature was lowered to 350 degrees C, it was checked that the thin film of an amorphous silicon can be formed.

[0061] Moreover, it was checked by using the same approach as an example 1 that the silicon thin film of p mold or n mold can be formed. Furthermore, by repeating and applying the formation approach of the above silicon thin films, the multilayer silicon thin film was formed and the solar battery shown in drawing 6 was produced. It sets to drawing 6 and is SiO<sub>2</sub> on the alumina substrate 41. The film 42 and Si<sub>3</sub>N<sub>4</sub> The laminating of the film 43 is carried out one by one. This Si<sub>3</sub>N<sub>4</sub> On the film 43, p mold polycrystalline silicon layer 44 of boron addition with a thickness of 10 micrometers is formed. n mold diffusion layer 45 is formed by performing Lynn diffusion in this p mold polycrystalline silicon layer 44. The ITO electrode 46 is formed on this n mold diffusion layer 45. Furthermore, the aluminum electrode 47 is formed on p mold polycrystalline silicon layer 44 exposed after mesa etching. The solar-battery property was observed also in this component.

[0062] The single dimension chain poly germane (molecular weight 3000 [ about ]) or annular poly germane who becomes a source of example 5 germanium and to whom it is expressed with -(GeEt<sub>2</sub>) n- as a compound was used. At a room temperature, these compounds are solid-states and dissolve in organic solvents, such as a xylene.

[0063] The solution which dissolved these poly germane in the xylene was applied on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, the xylene was evaporated, the pyrolysis of the poly germane was carried out at 550 more degrees C, and germanium was separated. Consequently, it was checked that the thin film of polycrystal germanium is formed on a substrate.

[0064] Moreover, when passed hydrogen by the flow rate of 2m<sup>2</sup> / min, a pressure was set as 1atm, UV irradiation was added with the output of 10J using a KrF excimer laser and pyrolysis temperature was lowered to 200 degrees C, it was checked that the thin film of amorphous germanium can be formed.

[0065] The single dimension chain poly germane (molecular weight 1000 [ about ]) or annular poly germane who becomes a source of germanium and to whom it is expressed with -(GeH<sub>2</sub>) n- as a compound was used using the single dimension chain polysilane (molecular weight 1000 [ about ]) or annular polysilane used as the source of example 6 silicon expressed with -(SiH<sub>2</sub>) n- as a compound. At a room temperature, these compounds are solid-states and dissolve in organic solvents, such as a xylene.

[0066] The solution which dissolved these polysilane and the poly germane in the xylene independently, respectively was applied at a mixed predetermined rate on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, the xylene was evaporated, the pyrolysis of polysilane and the poly germane was carried out at 650 more degrees C, and silicon and germanium were separated. Consequently, it was checked that the thin film of the polycrystalline silicon-germanium corresponding to a raw material mole ratio is mostly formed on a substrate.

[0067] Moreover, when passed hydrogen by the flow rate of 2m<sup>2</sup> / min, a pressure was set as 1atm, UV irradiation was added with the output of 10J using a KrF excimer laser and pyrolysis temperature was lowered to 350 degrees C, it was checked that the thin film of amorphous silicon-germanium can be formed.

[0068] As a result of carrying out the laminating of Si thin film and the SiGe mixing thin film combining the above approaches, adding a donor and an acceptor in each layer and forming np junction, it became clear that a solar-battery property is shown.

[0069] It is P(SiMe<sub>3</sub>) 3 as a compound used as the single dimension chain polysilane (molecular weight 12000 [ about ]) expressed with -(SiHPh) n- as a compound used as the source of example 7 silicon, and the source of n mold impurity. It used. After carrying out the spin coat of the toluene solution of the mixture of these compounds on a quartz substrate, the vacuum drying was carried out at 70 degrees C for 1 hour. Subsequently, to the bottom of the mixed air

current of an argon and hydrogen, it heated at 700 degrees C by 300 degrees C for 1 hour for 1 hour, and the pyrolysis of the raw material was carried out. Consequently, the silicon thin film with which Lynn was doped was formed.

[0070] Si<sub>5</sub> Cl<sub>12</sub> which is one sort of the compound called par chlorosilicane as a halogenide used as the source of example 8 silicon was used. The melting point is 345 degrees C and this compound dissolves in organic solvents, such as the petroleum ether.

[0071] The solution which dissolved this Si<sub>5</sub> Cl<sub>12</sub> in the petroleum ether was applied on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, the petroleum ether was evaporated, the pyrolysis of Si<sub>5</sub> Cl<sub>12</sub> was carried out at 450 more degrees C, and silicon was separated. Consequently, it was checked that the thin film of an amorphous silicon is formed on a substrate. Moreover, it was checked by raising heating temperature that the thin film of polycrystalline silicon can be formed.

[0072] Next, after the same spreading process as the above, as a result of carrying out the process which separates silicon by the pyrolysis in the hydrogen ambient atmosphere containing diboron hexahydride, it was checked that a p-type silicon thin film can be formed. Moreover, after the same spreading process as the above, as a result of carrying out the process which separates silicon by the pyrolysis in the hydrogen ambient atmosphere containing an arsine, it was checked that n mold silicon thin film can be formed. In addition, a phosphine may be used instead of an arsine.

[0073] Furthermore, the solar battery shown in drawing 4 using the formation approach of the above silicon thin films was produced. As a result of measuring photoelectromotive force and searching for conversion efficiency about the obtained solar battery, it is 8.5% and it was checked that the conversion efficiency which is equal compared with the conventional amorphous-silicon solar cell is acquired.

[0074] Si<sub>6</sub> Cl<sub>14</sub> was used as a halogenide used as the source of example 9 silicon. The melting point is 320 degrees C and this compound dissolves in organic solvents, such as the petroleum ether.

[0075] The solution which dissolved this Si<sub>6</sub> Cl<sub>14</sub> in the petroleum ether was applied on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, the petroleum ether was evaporated, the pyrolysis of Si<sub>6</sub> Cl<sub>14</sub> was carried out at 440 more degrees C, and silicon was separated. Consequently, it was checked that the thin film of an amorphous silicon is formed on a substrate. Moreover, it was checked by raising heating temperature that the thin film of polycrystalline silicon can be formed.

[0076] Moreover, it was checked by using the same approach as an example 8 that the silicon thin film of p mold or n mold can be formed. Furthermore, as a result of repeating these approaches, carrying out the laminating of n mold silicon thin film and the p-type silicon thin film and forming np junction, it was checked that a photoelectromotive-force property is shown.

[0077] Same Si<sub>5</sub> Cl<sub>12</sub> as having used in the example 8 as a halogenide used as the source of example 10 silicon was used. This Si<sub>5</sub> Cl<sub>12</sub> was applied by mechanical actuation at the temperature near the melting point on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, the petroleum ether was evaporated, the pyrolysis of Si<sub>5</sub> Cl<sub>12</sub> was carried out at 450 more degrees C, and silicon was separated. Consequently, it was checked that the thin film of an amorphous silicon is formed on a substrate. Moreover, it was checked by raising heating temperature that the thin film of polycrystalline silicon can be formed.

[0078] Moreover, it was checked by using the same approach as an example 8 that the silicon thin film of p mold or n mold can be formed. Furthermore, by repeating and applying the formation approach of the above silicon thin films, the multilayer silicon thin film was formed and the solar battery shown in drawing 5 was produced. As a result of measuring photoelectromotive force and searching for conversion efficiency about the obtained solar battery, it is 14% and it was checked that the conversion efficiency which is equal compared with the conventional amorphous-silicon solar cell is acquired.

[0079] Same Si<sub>6</sub> Cl<sub>14</sub> as having used in the example 9 as a halogenide used as the source of example 11 silicon was used. This Si<sub>6</sub> Cl<sub>14</sub> was applied by mechanical actuation at the

temperature near the melting point on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, the petroleum ether was evaporated, the pyrolysis of Si6 Cl14 was carried out at 440 more degrees C, and silicon was separated. Consequently, it was checked that the thin film of an amorphous silicon is formed on a substrate. Moreover, it was checked by raising heating temperature that the thin film of polycrystalline silicon can be formed.

[0080] Moreover, it was checked by using the same approach as an example 8 that the silicon thin film of p mold or n mold can be formed. Furthermore, by repeating and applying the formation approach of the above silicon thin films, the multilayer silicon thin film was formed and the solar battery shown in drawing 6 was produced. The solar-battery property was observed also in this component.

[0081] germanium5 Cl12 was used as a halogenide used as the source of example 12 germanium. This compound dissolves in organic solvents, such as the petroleum ether. The solution which dissolved this germanium5 Cl12 in the petroleum ether was applied on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, the petroleum ether was evaporated, the pyrolysis of germanium5 Cl12 was carried out at 400 more degrees C, and germanium was separated. Consequently, it was checked that the thin film of polycrystal germanium is formed on a substrate. Moreover, when UV irradiation was added and pyrolysis temperature was lowered, it was checked that the thin film of amorphous germanium can be formed.

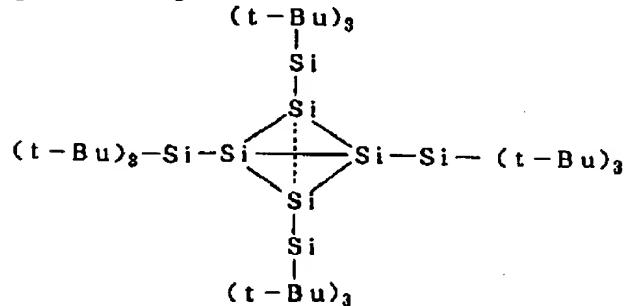
[0082] Si5 Br12 was used as a halogenide used as the source of example 13 silicon. This Si5 Br12 was applied by mechanical actuation at the temperature near the melting point on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, the petroleum ether was evaporated, the pyrolysis of Si5 Br12 was carried out at 440 more degrees C, and silicon was separated. Consequently, it was checked that the thin film of an amorphous silicon is formed on a substrate. Moreover, it was checked by raising heating temperature that the thin film of polycrystalline silicon can be formed.

[0083] Moreover, it was checked by using the same approach as an example 8 that the silicon thin film of p mold or n mold can be formed. Furthermore, by repeating and applying the formation approach of the above silicon thin films, the multilayer silicon thin film was formed and the solar battery shown in drawing 6 was produced. The solar-battery property was observed also in this component.

[0084] The solution which dissolved in the xylene the silane system compound shown with the following chemical formula as a source of example 14 silicon was applied on a silicon substrate, a quartz substrate, a glass substrate, or the stainless steel foil. These substrates are put into a hydrogen furnace, the xylene was evaporated, the pyrolysis of the silane system compound was carried out at 650 more degrees C, and silicon was separated. Consequently, it was checked that the thin film of polycrystalline silicon is formed on a substrate.

[0085]

[Formula 15]



[0086] Moreover, when passed hydrogen by the flow rate of 2m<sup>2</sup> / min, a pressure was set as 1atm, UV irradiation was added with the output of 10J using a KrF excimer laser and pyrolysis temperature was lowered to 350 degrees C, it was checked that the thin film of an amorphous silicon can be formed.

[0087] Next, after the same spreading process as the above, as a result of carrying out the process which separates silicon by the pyrolysis in the hydrogen ambient atmosphere containing diboron hexahydride, it was checked that a p-type silicon thin film can be formed. Moreover, after the same spreading process as the above, as a result of carrying out the process which separates silicon by the pyrolysis in the hydrogen ambient atmosphere containing an arsine, it was checked that n mold silicon thin film can be formed. In addition, a phosphine may be used instead of an arsine.

[0088] Furthermore, the solar battery shown in drawing 4 using the formation approach of the above silicon thin films was produced. As a result of measuring photoelectromotive force and searching for conversion efficiency about the obtained solar battery, it is 8.5% and it was checked that the conversion efficiency which is equal compared with the conventional amorphous-silicon solar cell is acquired.

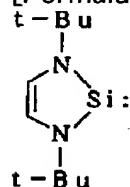
[0089] Similarly, the solar battery shown in drawing 5 was produced. As a result of measuring photoelectromotive force and searching for conversion efficiency about the obtained solar battery, it is 8.3% and it was checked that the conversion efficiency which is equal compared with the conventional amorphous-silicon solar cell is acquired.

[0090] Similarly, the solar battery shown in drawing 6 was produced. The solar-battery property was observed also in this component.

It is P(SiMe<sub>3</sub>)<sub>3</sub> as the silylene system compound shown with the following chemical formula as a compound used as the source of example 15 silicon, and a compound used as the source of n mold impurity. It used. After carrying out the spin coat of the toluene solution of the mixture of these compounds on a quartz substrate, the vacuum drying was carried out at 70 degrees C for 1 hour. Subsequently, to the bottom of the mixed air current of an argon and hydrogen, it heated at 600 degrees C by 300 degrees C for 1 hour for 1 hour, and the pyrolysis of the raw material was carried out. Consequently, the silicon thin film with which Lynn was doped was formed.

[0091]

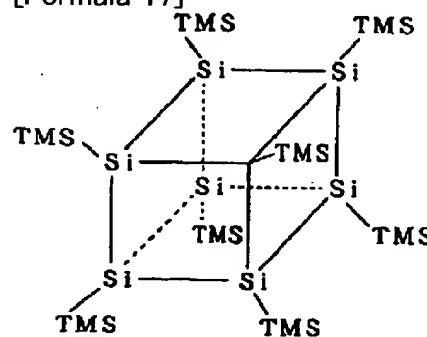
[Formula 16]



[0092] It is P(SiMe<sub>3</sub>)<sub>3</sub> as the OKUTASHIRA cubane compound which has the trimethylsilyl radical (TMS) shown with the following chemical formula as a compound used as the source of example 16 silicon, and a compound used as the source of n mold impurity. It used. After carrying out the spin coat of the toluene solution of the mixture of these compounds on a quartz substrate, the vacuum drying was carried out at 70 degrees C for 1 hour. Subsequently, to the bottom of the mixed air current of an argon and hydrogen, it heated at 600 degrees C by 300 degrees C for 1 hour for 1 hour, and the pyrolysis of the raw material was carried out. Consequently, the silicon thin film with which Lynn was doped was formed.

[0093]

[Formula 17]



---

[Translation done.]

**\* NOTICES \***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**DESCRIPTION OF DRAWINGS**

---

**[Brief Description of the Drawings]**

**[Drawing 1]** The mimetic diagram showing an example of the equipment for enforcing the approach of this invention.

**[Drawing 2]** The mimetic diagram showing other examples of the equipment for enforcing the approach of this invention.

**[Drawing 3]** The mimetic diagram showing the example of further others of the equipment for enforcing the approach of this invention.

**[Drawing 4]** The sectional view showing an example of the solar battery manufactured in the example of this invention.

**[Drawing 5]** The sectional view showing other examples of the solar battery manufactured in the example of this invention.

**[Drawing 6]** The sectional view showing the example of further others of the solar battery manufactured in the example of this invention.

**[Description of Notations]**

- 1 — Substrate
- 2 — Semi-conductor thin film
- 3 — Coater
- 4 — Nozzle
- 5 — Hydrogen furnace
- 6 — Heater
- 7 — Raw material container
- 8 — Semi-conductor raw material solution
- 11 — Supply roll
- 12 — Delivery roll
- 13 — Rolling-up roll
- 21 — Glass substrate
- 22 — Transparent electrode
- 23 — p mold amorphous silicon layer
- 24 — Undoping (i mold) amorphous silicon layer
- 25 — n mold amorphous silicon layer
- 26 — Aluminum electrode
- 27 — Aluminum electrode
- 31 — Stainless steel substrate
- 32 — Molybdenum electrode
- 33 — p mold amorphous silicon layer
- 34 — i mold amorphous silicon layer
- 35 — p mold amorphous silicon layer
- 36 — ITO electrode
- 37 — Aluminum electrode
- 41 — Alumina substrate
- 42 — SiO<sub>2</sub> Film

- 43 -- Si<sub>3</sub>N<sub>4</sub> Film
- 44 -- p mold polycrystalline silicon layer
- 45 -- n mold diffusion layer
- 46 -- ITO electrode
- 47 -- Aluminum electrode

---

[Translation done.]

(19)日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11)特許出願公開番号

特開平9-237927

(43)公開日 平成9年(1997)9月9日

(51)Int.Cl. <sup>8</sup>	識別記号	序内整理番号	F I	技術表示箇所
H 01 L 51/00			H 01 L 29/28	
C 23 C 18/08			C 23 C 18/08	
H 01 L 21/20			H 01 L 21/20	
21/368			21/368	L
31/04			31/04	V

審査請求 未請求 請求項の数4 O L (全13頁)

(21)出願番号	特願平8-247869	(71)出願人	000003078 株式会社東芝 神奈川県川崎市幸区堀川町72番地
(22)出願日	平成8年(1996)9月19日	(72)発明者	別府 達郎 神奈川県川崎市幸区小向東芝町1番地 株式会社東芝研究開発センター内
(31)優先権主張番号	特願平7-338877	(72)発明者	早瀬 修二 神奈川県川崎市幸区小向東芝町1番地 株式会社東芝研究開発センター内
(32)優先日	平7(1995)12月26日	(72)発明者	平岡 俊郎 神奈川県川崎市幸区小向東芝町1番地 株式会社東芝研究開発センター内
(33)優先権主張国	日本 (J P)	(74)代理人	弁理士 鈴江 武彦 (外6名)
(31)優先権主張番号	特願平7-338940		
(32)優先日	平7(1995)12月26日		
(33)優先権主張国	日本 (J P)		

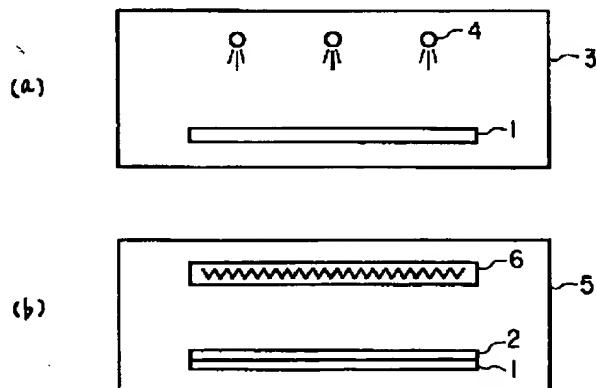
最終頁に続く

(54)【発明の名称】 半導体薄膜形成方法および太陽電池の製造方法

(57)【要約】

【課題】 大面積のシリコンで構成される半導体薄膜を容易に形成できる方法、およびこの方法を利用して大面積の太陽電池を製造する方法を提供する。

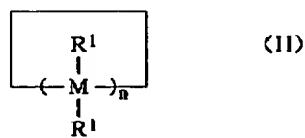
【解決手段】 一般式- $(S_i R^1 z)^n$ - (式中、Rは水素、 $\beta$ 位水素を有する炭素数2以上のアルキル基およびフェニル基、シリル基からなる群より選択される少なくとも1種)で表されるポリシランの溶液を基板上に塗布した後、熱分解してシリコンを遊離させる。



## 【特許請求の範囲】

【請求項1】 半導体原料の溶液を基板上に塗布した後、熱分解して半導体を遊離させて半導体薄膜を形成する方法であつて、前記半導体原料が、一般式(I)および(II)。

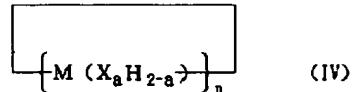
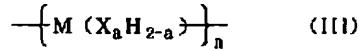
## 【化1】



(式中、Mはシリコンおよびゲルマニウムからなる群より選択され、R<sup>1</sup>は、それぞれ独立に、水素、β位水素を有する炭素数2以上のアルキル基およびフェニル基、シリル基からなる群より選択される。)で表される化合物、一般式(III)および(VI)。

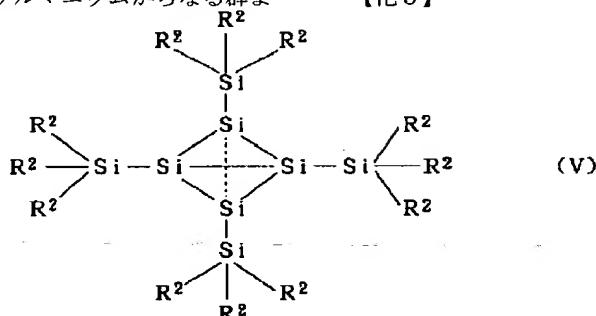
り選択され、R<sup>1</sup>は、それぞれ独立に、水素、β位水素を有する炭素数2以上のアルキル基およびフェニル基、シリル基からなる群より選択される。)で表される化合物、一般式(III)および(VI)。

## 【化2】



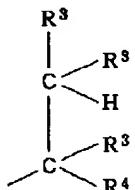
(式中、Mはシリコンおよびゲルマニウムからなる群より選択され、Xはハロゲン原子、nは4以上の整数、aは1または2である。)で表される化合物、一般式(V)。

## 【化3】



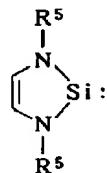
(式中、R<sup>2</sup>は、それぞれ独立に、下記式で表される置換または非置換のアルキル基、アリール基およびアラルキル基からなる群より選択される。)

## 【化4】



(式中、R<sup>3</sup>は、それぞれ独立に、水素原子、炭素数1～15の置換または非置換のアルキル基、炭素数6～15の置換または非置換のアリール基、および炭素数7～15の置換または非置換アラルキル基からなる群より選択され、R<sup>4</sup>は炭素数1～15の置換または非置換アルキル基、炭素数6～15の置換または非置換アリール基、および炭素数7～15の置換または非置換アラルキル基からなる群より選択される。)で表される化合物、ならびに一般式(VI)。

## 【化5】



(式中、R<sup>5</sup>は、それぞれ独立に、炭素数1～15の置換または非置換のアルキル基、アリール基、およびアラルキル基、ならびにケイ素数1～5の置換または非置換のシリル基からなる群より選択される。)で表される化合物からなる群より選択されることを特徴とする半導体薄膜形成方法。

【請求項2】 前記一般式(I)～(VI)で表される化合物からなる群より選択される半導体原料の溶液にp型またはn型の導電型を与えるドーパント源を添加して基板上に塗布した後、熱分解して所定導電型の不純物を含有する半導体を遊離させることを特徴とする半導体薄膜形成方法。

【請求項3】 前記一般式(I)～(VI)で表される化合物からなる群より選択される半導体原料の溶液を基板上に塗布した後、p型またはn型の導電型を与えるドーパント源を含有する雰囲気中で熱分解して所定導電型の不純物を含有する半導体を遊離させることを特徴とする半導体薄膜形成方法。

【請求項4】 1対の電極間に、i型、p型およびn型のうちいずれかの導電型を有する半導体薄膜を2層以上設けて半導体接合を形成した太陽電池を製造するにあたり、i型の半導体薄膜を形成する場合には、前記一般式(I)～(VI)で表される化合物からなる群より選択される半導体原料の溶液を塗布した後、熱分解して半導体を遊離させる工程を採用し、p型またはn型の半導体薄膜を形成する場合には、前記一般式(I)～(VI)で表される化合物からなる群より選択される半導体原料の溶液に所定導電型を与えるドーパント源を添加して基板上に塗布した後に熱分解するか、または前記一般式(I)～(VI)で表される化合物からなる群より選択される半導体原料の溶液を基板上に塗布した後に所定の導電型を与えるドーパント源を含有する雰囲気中で熱分解することにより、所定導電型を与える不純物を含有する半導体を遊離させる工程を採用し、これらの工程を繰り返して2層以上の半導体薄膜を形成することを特徴とする太陽電池の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は新規な半導体薄膜形成方法およびこの方法を利用した太陽電池の製造方法に関する。

【0002】

【従来の技術】 従来、IV族元素であるシリコンまたはゲルマニウムで構成される半導体薄膜を形成する方法としては、蒸着法、スパッタ法、イオンプレーティング法、CVD法などの気相成長法が用いられている。しかし、これらの方法はいずれも、成膜時に減圧環境、水素炉環境などを用いるため、気密性の高い反応容器を使用することが不可欠であり、大面積の基板上に均一な半導体薄膜を形成することが困難であった。このため、半導体薄膜を有する応用製品、例えば太陽電池でも、従来比で一桁以上面積の大きいものを製造するには限界があった。

【0003】 そこで、大面積の半導体薄膜を形成する方法の1つとして、湿式塗布法を用いることが考えられている。例えば特開平4-119996号公報には、基板上にシリコン源としてオクタシラキュバンなどの化合物を塗布し、このシリコン源化合物を熱分解することにより、シリコン薄膜を形成する方法が開示されている。この方法は、真空チャンバーのような大規模で高価な製造設備を必要とせず、大面積の基板上にシリコン薄膜を容易に形成するのに有利であると考えられている。

【0004】 しかし、この公報に記載されたオクタシラキュバンなどの化合物は酸素に対して不安定であることが多く、空气中で容易に酸化されて変性する。また、これらの化合物は溶媒への溶解性が低いことが多く、均一な薄膜を形成することが困難である。

【0005】 さらに、太陽電池などへの応用を考慮すると、p型またはn型の不純物をドープしたシリコン薄膜

を形成する必要がある。しかし、従来は熱分解によりシリコン薄膜を形成した後に、熱拡散やイオン注入により不純物のドーピングを行っているため、大規模な装置を必要とし、工程の複雑化を招いていた。

【0006】

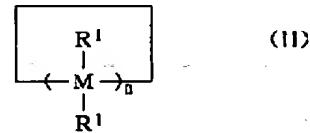
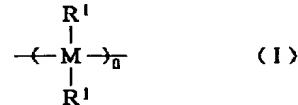
【発明が解決しようとする課題】 本発明の目的は、大面積のシリコンまたはゲルマニウムで構成される半導体薄膜を容易に形成できる方法、およびこの方法を利用して大面積の太陽電池を製造する方法を提供することにある。

【0007】

【課題を解決するための手段】 本発明の半導体薄膜形成方法は、半導体原料の溶液を基板上に塗布した後、熱分解して半導体を遊離させて半導体薄膜を形成する方法であって、前記半導体原料が、一般式(I)および(II)

【0008】

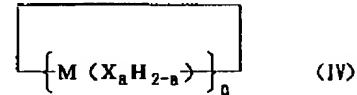
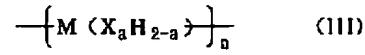
【化6】



(式中、Mはシリコンおよびゲルマニウムからなる群より選択され、R¹は、それぞれ独立に、水素、β位水素を有する炭素数2以上のアルキル基およびフェニル基、シリル基からなる群より選択される。) で表される化合物、一般式(III)および(IV)

【0009】

【化7】

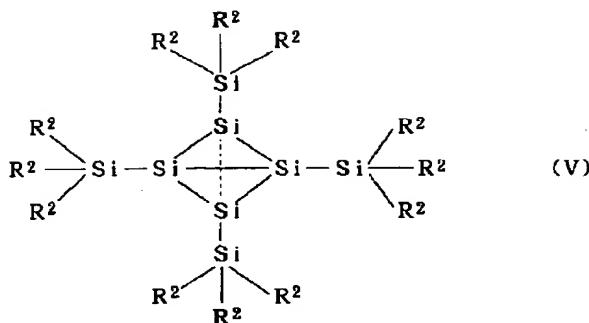


(式中、Mはシリコンおよびゲルマニウムからなる群より選択され、Xはハロゲン原子、nは4以上の整数、aは1または2である。) で表される化合物、一般式(V)

【0010】

【化8】

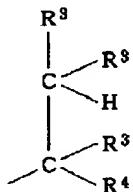
5



(式中、R<sup>2</sup> は、それぞれ独立に、下記式で表される置換または非置換のアルキル基、アリール基およびアラルキル基からなる群より選択される。)

【0011】

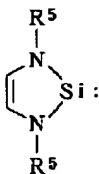
【化9】



(式中、R<sup>3</sup> は、それぞれ独立に、水素原子、炭素数1～15の置換または非置換のアルキル基、炭素数6～15の置換または非置換のアリール基、および炭素数7～15の置換または非置換アラルキル基からなる群より選択され、R<sup>4</sup> は炭素数1～15の置換または非置換アルキル基、炭素数6～15の置換または非置換アリール基、および炭素数7～15の置換または非置換アラルキル基からなる群より選択される。) で表される化合物、ならびに一般式 (VI)

【0012】

【化10】



(式中、R<sup>5</sup> は、それぞれ独立に、炭素数1～15の置換または非置換のアルキル基、アリール基、およびアラルキル基、ならびにケイ素数1～5の置換または非置換のシリル基からなる群より選択される。) で表される化合物からなる群より選択されるものである。

【0013】本発明における、所定導電型を有する半導体薄膜の形成方法は、前記一般式 (I) ～ (VI) で表される化合物からなる群より選択される半導体原料の溶液にp型またはn型の導電型を与えるドーパント源を添加して基板上に塗布した後、熱分解して所定導電型の不純物を含有する半導体を遊離させるものである。

6

【0014】本発明における、所定導電型を有する半導体薄膜の他の形成方法は、前記一般式 (I) ～ (VI) で表される化合物からなる群より選択される半導体原料の溶液を基板上に塗布した後、p型またはn型の導電型を与えるドーパント源を含有する雰囲気中で熱分解して所定導電型の不純物を含有する半導体を遊離させるものである。

【0015】本発明の太陽電池の製造方法は、1対の電極間に、i型、p型およびn型のうちいずれかの導電型を有する半導体薄膜を2層以上設けて半導体接合を形成した太陽電池を製造するにあたり、i型の半導体薄膜を形成する場合には、前記一般式 (I) ～ (VI) で表される化合物からなる群より選択される半導体原料の溶液を基板上に塗布した後、熱分解して半導体を遊離させる工程を採用し、p型またはn型の半導体薄膜を形成する場合には、前記一般式 (I) ～ (VI) で表される化合物からなる群より選択される半導体原料の溶液に所定導電型を与えるドーパント源を添加して基板上に塗布した後に熱分解するか、または前記一般式 (I) ～ (VI) で表される化合物からなる群より選択される半導体原料の溶液を基板上に塗布した後に所定の導電型を与えるドーパント源を含有する雰囲気中で熱分解することにより、所定導電型を与える不純物を含有する半導体を遊離させる工程を採用し、これらの工程を繰り返して2層以上の半導体薄膜を形成するものである。

【0016】

【発明の実施の形態】以下、本発明をさらに詳細に説明する。本発明において、基板材料としては、シリコンなどの半導体、ガラス、透明電極を有するガラス、金属、セラミックス、耐熱性高分子などから選択される任意の材料を用いることができる。

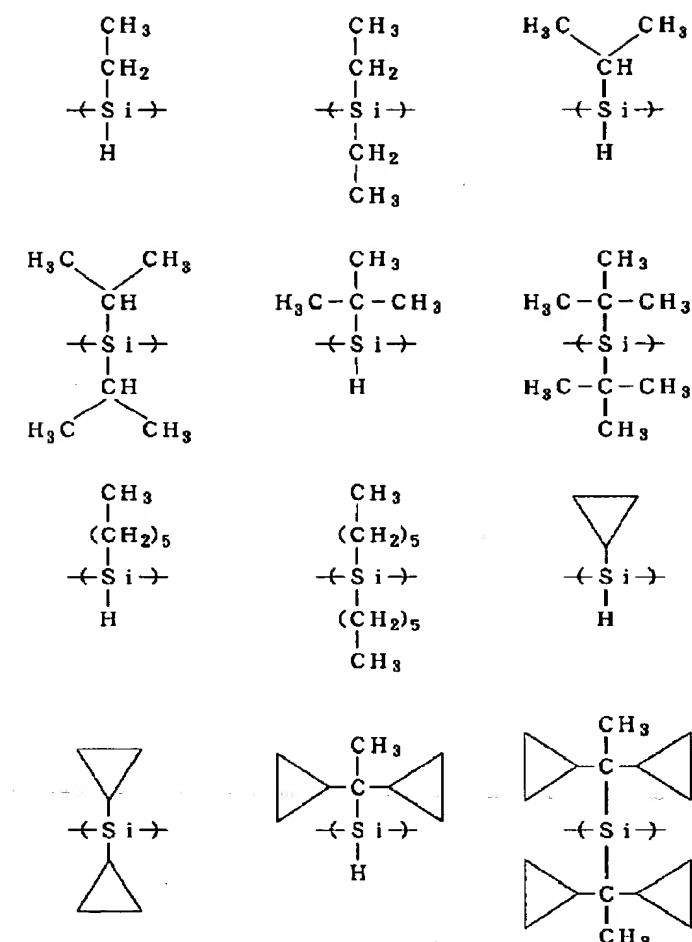
【0017】本発明において用いられる、半導体原料となる化合物について説明する。一般式 (I) または (II) で表される化合物は、一次元鎖または環状構造をなすシラン系またはゲルマン系化合物である。これらの化合物は共重合体でもよいし、混合物として用いてもよい。本発明においては、室温で固体であり、有機溶媒に可溶な化合物が用いられる。このような条件を満たすためには、例えば一次元鎖構造を有するポリマーでは重合度nが3以上10000以下であることが好ましく、さらに5～30であることがより好ましい。

【0018】一般式 (I) または (II) で表される化合物の具体例を以下に示す。なお、以下においては一次元鎖のポリシランのみを示すが、環状ポリシランでもよく、シリコンをゲルマニウムに置き換えたポリゲルマンでもよいことはもちろんである。

【0019】

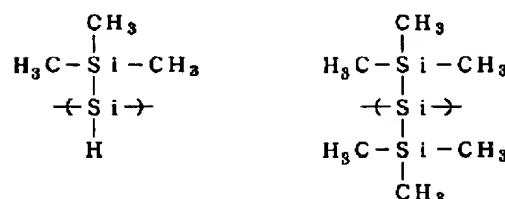
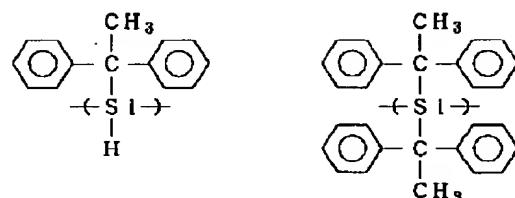
【化11】

7

【0020】  
【化12】

30

40



物は、シリコンまたは/およびゲルマニウムのハロゲン化物である。これらのハロゲン化物は、有機溶媒に可溶という条件を満たすためには、重量平均分子量が500～10万であることが好ましい。分子量が小さいと熱分解が起こらないうちに基板上から揮発するため、良好な膜が形成されにくい。分子量が上記の範囲であれば、熱分解温度での蒸気圧が比較的低く、基板からの揮発を無視できる。分子量が大きすぎると溶媒に対する溶解性が低下し、基板への塗布が困難になる。

【0022】一般式(V)で表されるシラン系化合物は、室温で固体であり、有機溶媒に可溶であり、酸化に対する安定性が高い。一般式(VI)で表されるシリレン化合物は、室温で固体であり、有機溶媒に可溶であり、酸化に対する安定性が高い。

【0023】本発明において用いられる一般式(I)～(VI)で表される化合物は有機溶媒に可溶であるので、ディッピング、スピンドルコーティング、スプレーコーティングなど任意の塗布法により大面積の平面または曲面を持つ基板上に塗布して均一な塗膜を形成できる。塗膜の膜厚は、数十nmであることが好ましい。この塗布工程で用いられる器具は基板の大きさに応じて任意に選択できる。また、塗布装置に関しては大気の混入を防止できれば十分であり、気相成長法の場合のような気密性の高い大規模な減圧装置は不要である。

【0024】本発明においては、基板上に塗布された化合物の塗膜を、所定の雰囲気、例えば不活性ガス雰囲気または水素などの還元性雰囲気中において、その融点前後まで加熱して溶媒を蒸発させた後、熱分解反応を起させることにより、シリコンまたは/およびゲルマニウムを遊離させて半導体薄膜を形成する。雰囲気の圧力は常圧(1気圧)前後でよい。また、反応生成物は排気により除去することが好ましい。加熱手段は特に限定されず、一般的な電気炉を用いてもよいし、ラピッドサーマルアニーリング法のように赤外線を照射してもよいし、レーザーアニールを行ってもよい。具体的な熱分解温度は化合物によって異なる。例えば、一般式(I)および(II)で表される化合物の場合には、200～700℃、さらに300～650℃で熱分解を実施することが好ましい。一般式(III)および(IV)で表される化合物の場合には、約250℃～約1300℃の範囲で熱分解が起こるが、300～500℃で熱分解を実施することが好ましい。一般式(V)および(VI)で表される化合物の場合には、300～700℃で熱分解を実施することが好ましい。昇温速度は5℃/min程度に設定される。反応時間は10分～10時間で十分である。ただし、場合によっては昇温せず、一定温度での熱分解を行ってもよい。

【0025】この熱分解反応により、半導体原料の側鎖に導入されている置換基の脱離反応が起こる。例えば、 $\beta$ 位水素を有する炭素数2以上のアルキル基を有する化

合物では $\beta$ 脱離反応が起こり、フェニル基を有する化合物ではラジカル脱離が起こる。このような熱分解反応によりシリコンまたはゲルマニウムの多結晶薄膜を形成できる。また、紫外線照射による分解を併用し、熱分解温度を低下させればアモルファス薄膜を形成できる。なお、これらの薄膜は、IV族元素以外に若干の水素を含むものである。

【0026】シラン系化合物とゲルマン系化合物との混合物の溶液、またはシランの繰り返し単位とゲルマンの繰り返し単位とを有する共重合体の溶液を塗布し、熱分解させることにより、シリコンとゲルマニウムとの混合半導体薄膜を形成することもできる。なお、シリコンとゲルマニウムとの組成を制御するには前者の方法の方が好ましい。

【0027】上記のような本発明の方法を実施するための装置を図1～図3に模式的に示す。図1(a)に示すように、ノズル4を備えた塗布装置3内に基板1を入れて、塗布装置3内への大気混入を防止するために窒素ガス雰囲気とした後、ノズル4から半導体原料の溶液を噴霧して基板1上に塗布する。この場合、ノズル形状および噴霧時間を適宜設定することにより、基板1上に塗布される溶液の量を制御することができる。次に、図1(b)に示すように、半導体原料の溶液が塗布された基板1を水素炉5に入れ、水素を主体とする還元性ガス雰囲気中でヒーター6により基板1を加熱して半導体原料を熱分解させ、基板1上に半導体薄膜2を形成する。なお、ヒーター6としては赤外線ヒーター、抵抗加熱ヒーターなどを用いることができる。

【0028】図2に示すように、水素炉5内に基板1を入れ、基板1上にノズル4から半導体原料の溶液を直接噴霧して基板1上に塗布し、基板1をヒーター6によって加熱し、半導体原料を熱分解することにより半導体薄膜を形成することもできる。

【0029】また、図3はフレキシブルな基板を用いて連続的に半導体薄膜を製造するための装置を示すものである。フレキシブルな基板1は供給ロール11から供給されて原料容器7内の半導体原料溶液8に浸漬される。基板1は送りロール12、12により水素炉5へ送られる。水素炉5内でヒーター6により加熱されて半導体原料の熱分解が行われ、基板1上に半導体薄膜が形成される。その後、基板1は巻き取りロール13に巻き取られる。このようにしてフレキシブルな基板上に連続的に半導体薄膜を形成することができる。

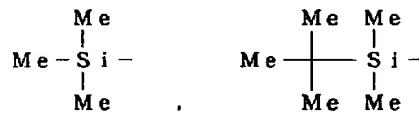
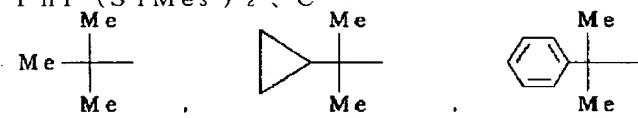
【0030】本発明においては、p型またはn型の導電型を与えるドーパント源を用いることにより、所定導電型の半導体薄膜を形成することもできる。その方法としては以下のよう2つの方法を用いることができる。すなわち、(1)一般式(I)～(VI)で表される化合物からなる群より選択される半導体原料の溶液にp型またはn型の導電型を与えるドーパント源を添加して基板上

に塗布した後、熱分解して所定導電型の不純物を含有する半導体を遊離させる方法、および(2)一般式(I)～(VI)で表される化合物からなる群より選択される半導体原料の溶液を基板上に塗布した後、p型またはn型の導電型を与えるドーパント源を含有する雰囲気中で熱分解して所定導電型の不純物を含有する半導体を遊離させる方法である。これらの方法を実施するための装置および反応条件は、先に記載したのと同様でよい。

【0031】これらの方法において、p型不純物としては一般的にホウ素(B)が、n型不純物としてはリン(P)、ヒ素(As)、アンチモン(Sb)が用いられる。(1)の方法では、ドーパント源として不純物元素のアルキル化物、または分子内に不純物元素とSiとの結合を有する化合物が用いられる。(2)の方法では、ドーパント源として不純物元素のアルキル化物、分子内に不純物元素とSiとの結合を有する化合物、または不純物元素の水素化物が用いられる。半導体原料に対するドーパント源の添加量は、形成すべき半導体薄膜に必要な不純物濃度によるが、一般的には、原料中の全ケイ素原子数に対する不純物元素の原子数が0.1～10%であることが好ましい。

【0032】p型不純物のアルキル化物としては、例えばBPh<sub>3</sub>、BMePh<sub>2</sub>、B(t-Bu)<sub>3</sub>などが挙げられる。p型不純物とSiとの結合を有する化合物としては、B(SiMe<sub>3</sub>)<sub>3</sub>、PhB(SiMe<sub>3</sub>)<sub>2</sub>、Cl<sub>2</sub>B(SiMe<sub>3</sub>)などが挙げられる。p型不純物の水素化物としては例えびジボランなどが挙げられる。

【0033】n型不純物のアルキル化物としては、例えばPPh<sub>3</sub>、PMePh<sub>2</sub>、P(t-Bu)<sub>3</sub>、AsPh<sub>3</sub>、AsMePh<sub>2</sub>、As(t-Bu)<sub>3</sub>、SbPh<sub>3</sub>、SbMePh<sub>2</sub>、Sb(t-Bu)<sub>3</sub>などが挙げられる。n型不純物とSiとの結合を有する化合物としては、P(SiMe<sub>3</sub>)<sub>3</sub>、PhP(SiMe<sub>3</sub>)<sub>2</sub>、C



【0038】これらの置換基のうち、特にトリメチルシリル基(Me<sub>3</sub>Si-)を有するオクタシラキュバンは有機溶媒に対する溶解性が良好であるため好ましい。さらに、本発明においては上述したような半導体薄膜の形成方法を利用して大面積の太陽電池を製造することができる。すなわち、太陽電池は1対の電極間にi型、p型およびn型のうちいずれかの導電型を有する半導体薄膜

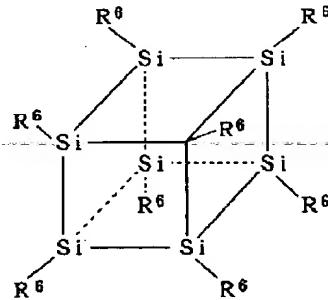
12P(SiMe<sub>3</sub>)、As(SiMe<sub>3</sub>)<sub>3</sub>、PhAs(SiMe<sub>3</sub>)<sub>2</sub>、Cl<sub>2</sub>As(SiMe<sub>3</sub>)Sb(SiMe<sub>3</sub>)<sub>3</sub>、PhSb(SiMe<sub>3</sub>)<sub>2</sub>、Cl<sub>2</sub>Sb(SiMe<sub>3</sub>)などが挙げられる。n型不純物の水素化物としては例えびホスフィン、アルシンなどが挙げられる。

【0034】上記のドーパント源のうち、特にB-Si結合を有する化合物またはP(AsもしくはSb)-Si結合を有する化合物を用いた場合、これらの化合物中には不純物とCとの結合が少ないため、形成される半導体薄膜中に取り込まれるCの量を抑制することができ、半導体薄膜の電気的特性を改善できる。

【0035】なお、ドーパント源としてB-Si結合を有する化合物またはP(AsもしくはSb)-Si結合を有する化合物を用いる場合、シリコン源となる化合物として、下記一般式で表されるオクタシラキュバンを用いることもできる。

【0036】

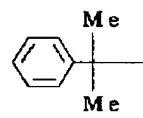
【化13】



30置換基R<sup>6</sup>の具体例としては下記に示すようなものが挙げられる。

【0037】

【化14】



を2層以上設けて半導体接合を形成した構造を有するので、上述した方法を繰り返して2層以上の半導体薄膜を形成することにより、p-n、p-i-n、i-p、i-nなどの半導体接合を実現することができる。

【0039】本発明の方法により太陽電池を製造する場合、例えび図3に示したような原料容器と水素炉の組み合わせを複数セット連結することにより、多層の半導体

薄膜を一貫した連続工程で積層成膜でき、大面積の太陽電池の製造に有利である。

【0040】以上のように、本発明では最初に半導体原料の溶液を塗布し、その後に熱分解により半導体を遊離させてるので、基板が大面積であっても均一な半導体薄膜を形成でき、さらにこのような方法を利用して大面積の太陽電池を製造できる。

【0041】なお、本発明の方法は太陽電池の製造を主目的に開発されたが、大面積のアモルファスシリコン TFT の製造にも有効なことは明らかである。また、本発明の方法は曲面を持つ基板に対しても適用可能であることから、他の分野への応用も期待できる。

#### 【0042】

【実施例】以下、本発明の実施例を説明する。

##### 実施例1

テトラヒドロフラン中にジクロロシランを溶解し、金属リチウムを加えて所定の重合条件で重合させて—(SiH<sub>2</sub>)<sub>n</sub>—で表される一次元鎖ポリシランを合成し、固体として析出させた。得られた一次元鎖ポリシランは、nが5～15のポリシランの混合物であった。このポリシランは室温では固体であり、キシレンなどの有機溶媒に溶解する。

【0043】このポリシランをキシレンに溶解した溶液を、シリコン基板、石英基板、ガラス基板またはステンレスフォイル上に塗布した。これらの基板を水素炉に入れ、キシレンを蒸発させ、さらに650℃でポリシランを熱分解させてシリコンを遊離させた。この結果、基板上に多結晶シリコンの薄膜が形成されていることが確認された。

【0044】また、水素を2m<sup>2</sup>/minの流量で流して圧力を1atmに設定し、KrFエキシマレーザーを使用して10Jの出力で紫外線照射を加えて熱分解温度を350℃に下げた場合には、アモルファスシリコンの薄膜を形成できることが確認された。

【0045】次に、上記と同様な塗布工程の後、熱分解によりシリコンを遊離させる工程をジボランを含有する水素雰囲気中で実施した結果、p型シリコン薄膜を形成できることが確認された。また、上記と同様な塗布工程の後、熱分解によりシリコンを遊離させる工程をアルシンを含有する水素雰囲気中で実施した結果、n型シリコン薄膜を形成できることが確認された。なお、アルシンの代わりにホスフィンを用いてもよい。

【0046】さらに、以上のようなシリコン薄膜の形成方法を利用して図4に示す太陽電池を作製した。図4において、ガラス基板21上には、酸化錫(SnO<sub>2</sub>)または酸化インジウム錫(ITO)からなる透明電極22が形成されている。この透明電極22上には、透明電極22の一部が露出するようにポリシラン溶液を塗布し熱分解する工程を繰り返すことにより、厚さ0.1μmのp型アモルファスシリコン層23、厚さ0.5μmのア

ンドープ(i型)アモルファスシリコン層24、および厚さ0.1μmのn型アモルファスシリコン層25が順次積層されている。さらに、n型アモルファスシリコン層25上にはアルミニウム電極26が、露出した透明電極22上にはアルミニウム電極27がそれぞれ形成されている。

【0047】得られた太陽電池について、光起電力を測定して変換効率を求めた結果、7.8%であり、従来のアモルファスシリコン太陽電池に比べて遜色のない変換効率が得られることが確認された。

#### 【0048】実施例2

Arで満たされた反応容器に1Lのトルエンを加え、この中に細かく裁断した金属Na 2.2モルを加えた。1モルのジエチルジクロロシランと0.05モルのトリエチルクロロシランとの混合液を100mLのトルエンで希釈した溶液を上記反応容器に1時間にわたって滴下した。この際、反応温度が100℃を越えないように滴下速度をコントロールした。滴下終了後、さらに2時間、110℃で反応させた。その後、未反応の金属をエタノールで処理した後、一次元鎖ポリシランをエタノール中に沈殿させた。このポリシランは—(SiEt<sub>2</sub>)<sub>n</sub>—で表され、分子量は約3000であった。

【0049】このポリシランをキシレンに溶解した溶液を、シリコン基板、石英基板、ガラス基板またはステンレスフォイル上に塗布した。これらの基板を水素炉に入れ、キシレンを蒸発させ、さらに450℃でポリシランを熱分解させてシリコンを遊離させた。この結果、基板上に多結晶シリコンの薄膜が形成されていることが確認された。

【0050】また、水素を2m<sup>2</sup>/minの流量で流して圧力を1atmに設定し、KrFエキシマレーザーを使用して10Jの出力で紫外線照射を加えて熱分解温度を350℃に下げた場合には、アモルファスシリコンの薄膜を形成できることが確認された。

【0051】また、実施例1と同様な方法を用いることによりp型またはn型のシリコン薄膜を形成できることが確認された。さらに、これらの方法を繰り返し、n型シリコン薄膜およびp型シリコン薄膜を積層してn-p接合を形成した結果、光起電力特性を示すことが確認された。

【0052】なお、置換基Rが—CH(CH<sub>3</sub>)<sub>2</sub>、—C(CH<sub>3</sub>)<sub>3</sub>、—C(CH<sub>3</sub>)Ph<sub>2</sub>または—C(CH<sub>3</sub>)<sub>2</sub>cyclopropyl<sub>2</sub>であるポリシランを用いた場合にも良好な結果が得られた。

#### 【0053】実施例3

シリコン源となる化合物として—(SiEtPh)<sub>n</sub>—で表される一次元鎖ポリシラン(分子量約5000)を用いた。このポリシランは室温では固体であり、キシレンなどの有機溶媒に溶解する。

【0054】このポリシランをキシレンに溶解した溶液

を、シリコン基板、石英基板、ガラス基板またはステンレスフォイル上に塗布した。これらの基板を水素炉に入れ、キシレンを蒸発させ、さらに450°Cでポリシランを熱分解させてシリコンを遊離させた。この結果、基板上に多結晶シリコンの薄膜が形成されていることが確認された。

【0055】また、水素を2m<sup>2</sup>/minの流量で流して圧力を1atmに設定し、KrFエキシマレーザーを使用して10Jの出力で紫外線照射を加えて熱分解温度を370°Cに下げた場合には、アモルファスシリコンの薄膜を形成できることが確認された。

【0056】また、実施例1と同様な方法を用いることによりp型またはn型のシリコン薄膜を形成できることが確認された。さらに、以上のようなシリコン薄膜の形成方法を繰り返して適用することにより多層のシリコン薄膜を形成し、図5に示す太陽電池を作製した。図5において、ステンレス基板31上には、モリブデン電極32が形成されている。このモリブデン電極32上には、厚さ0.1μmのp型アモルファスシリコン層33、厚さ0.4μmのi型アモルファスシリコン層34、および厚さ0.1μmのp型アモルファスシリコン層35が順次形成されている。さらに、p型アモルファスシリコン層35上にはITO電極36およびアルミニウム電極37が順次形成されている。

【0057】得られた太陽電池について、光起電力を測定して変換効率を求めた結果、8.3%であり、従来のアモルファスシリコン太陽電池に比べて遜色のない変換効率が得られることが確認された。

#### 【0058】実施例4

シリコン源となる化合物として(Si(t-Bu)<sub>2</sub>)<sub>n</sub>(nは3または4)で表される環状ポリシランを用いた。この環状ポリシランは室温では固体であり、トルエンなどの有機溶媒に溶解する。

【0059】この環状ポリシランをトルエンに溶解した溶液を、シリコン基板、石英基板、ガラス基板またはステンレスフォイル上に塗布した。これらの基板を水素炉に入れ、トルエンを蒸発させ、さらに430°Cで環状ポリシランを熱分解させてシリコンを遊離させた。この結果、基板上に多結晶シリコンの薄膜が形成されていることが確認された。

【0060】また、水素を2m<sup>2</sup>/minの流量で流して圧力を1atmに設定し、KrFエキシマレーザーを使用して10Jの出力で紫外線照射を加えて熱分解温度を350°Cに下げた場合には、アモルファスシリコンの薄膜を形成できることが確認された。

【0061】また、実施例1と同様な方法を用いることによりp型またはn型のシリコン薄膜を形成できることが確認された。さらに、以上のようなシリコン薄膜の形成方法を繰り返して適用することにより多層のシリコン薄膜を形成し、図6に示す太陽電池を作製した。図6に

おいて、アルミナ基板41上には、SiO<sub>2</sub>膜42およびSi<sub>3</sub>N<sub>4</sub>膜43が順次積層されている。このSi<sub>3</sub>N<sub>4</sub>膜43上に、厚さ10μmのボロン添加のp型多結晶シリコン層44が形成されている。このp型多結晶シリコン層44にリン拡散を行うことによりn型拡散層45が形成されている。このn型拡散層45上にITO電極46が形成されている。さらに、メサエッティング後に露出したp型多結晶シリコン層44上にアルミニウム電極47が形成されている。この素子においても、太陽電池特性が観測された。

#### 【0062】実施例5

ゲルマニウム源となる化合物として-(GeEt<sub>2</sub>)<sub>n</sub>で表される一次元鎖ポリゲルマン(分子量約3000)または環状ポリゲルマンを用いた。これらの化合物は室温では固体であり、キシレンなどの有機溶媒に溶解する。

【0063】これらのポリゲルマンをキシレンに溶解した溶液を、シリコン基板、石英基板、ガラス基板またはステンレスフォイル上に塗布した。これらの基板を水素炉に入れ、キシレンを蒸発させ、さらに550°Cでポリゲルマンを熱分解させてゲルマニウムを遊離させた。この結果、基板上に多結晶ゲルマニウムの薄膜が形成されていることが確認された。

【0064】また、水素を2m<sup>2</sup>/minの流量で流して圧力を1atmに設定し、KrFエキシマレーザーを使用して10Jの出力で紫外線照射を加えて熱分解温度を200°Cに下げた場合には、アモルファスゲルマニウムの薄膜を形成できることが確認された。

#### 【0065】実施例6

シリコン源となる化合物として-(SiH<sub>2</sub>)<sub>n</sub>で表される一次元鎖ポリシラン(分子量約1000)または環状ポリシランを用い、ゲルマニウム源となる化合物として-(GeH<sub>2</sub>)<sub>n</sub>で表される一次元鎖ポリゲルマン(分子量約1000)または環状ポリゲルマンを用いた。これらの化合物は室温では固体であり、キシレンなどの有機溶媒に溶解する。

【0066】これらのポリシランおよびポリゲルマンをそれぞれ独立にキシレンに溶解した溶液を、所定の混合割合でシリコン基板、石英基板、ガラス基板またはステンレスフォイル上に塗布した。これらの基板を水素炉に入れ、キシレンを蒸発させ、さらに650°Cでポリシランおよびポリゲルマンを熱分解させてシリコンおよびゲルマニウムを遊離させた。この結果、基板上に原料モル比にはほぼ対応する多結晶シリコン-ゲルマニウムの薄膜が形成されていることが確認された。

【0067】また、水素を2m<sup>2</sup>/minの流量で流して圧力を1atmに設定し、KrFエキシマレーザーを使用して10Jの出力で紫外線照射を加えて熱分解温度を350°Cに下げた場合には、アモルファスシリコン-ゲルマニウムの薄膜を形成できることが確認された。

【0068】以上のような方法を組み合わせてSi薄膜およびSiGe混合薄膜を積層し、それぞれの層にドナーおよびアクセプターを添加してn-p接合を形成した結果、太陽電池特性を示すことが明らかになった。

【0069】実施例7

シリコン源となる化合物として-(SiHPh)<sub>n</sub>で表される一次元鎖ポリシラン(分子量約12000)、およびn型不純物源となる化合物としてP(SiMe<sub>3</sub>)<sub>3</sub>を用いた。これらの化合物の混合物のトルエン溶液を石英基板上にスピンドルコートした後、70°Cで1時間真空乾燥した。次いで、アルゴンと水素との混合気流下において、300°Cで1時間、700°Cで1時間加熱して、原料を熱分解させた。この結果、リンがドープされたシリコン薄膜が形成された。

【0070】実施例8

シリコン源となるハロゲン化物としてパークロロシランと呼ばれる化合物の1種であるSi<sub>5</sub>C<sub>12</sub>を用いた。この化合物は、融点が345°Cであり、石油エーテルなどの有機溶媒に溶解する。

【0071】このSi<sub>5</sub>C<sub>12</sub>を石油エーテルに溶解した溶液を、シリコン基板、石英基板、ガラス基板またはステンレスフォイル上に塗布した。これらの基板を水素炉に入れ、石油エーテルを蒸発させ、さらに450°CでSi<sub>5</sub>C<sub>12</sub>を熱分解させてシリコンを遊離させた。この結果、基板上にアモルファスシリコンの薄膜が形成されていることが確認された。また、加熱温度を上げることにより多結晶シリコンの薄膜を形成できることが確認された。

【0072】次に、上記と同様な塗布工程の後、熱分解によりシリコンを遊離させる工程をジボランを含有する水素雰囲気中で実施した結果、p型シリコン薄膜を形成できることが確認された。また、上記と同様な塗布工程の後、熱分解によりシリコンを遊離させる工程をアルシンを含有する水素雰囲気中で実施した結果、n型シリコン薄膜を形成できることが確認された。なお、アルシンの代わりにホスフィンを用いてもよい。

【0073】さらに、以上のようなシリコン薄膜の形成方法を利用して図4に示す太陽電池を作製した。得られた太陽電池について、光起電力を測定して変換効率を求めた結果、8.5%であり、従来のアモルファスシリコン太陽電池に比べて遜色のない変換効率が得られることが確認された。

【0074】実施例9

シリコン源となるハロゲン化物としてSi<sub>6</sub>C<sub>14</sub>を用いた。この化合物は、融点が320°Cであり、石油エーテルなどの有機溶媒に溶解する。

【0075】このSi<sub>6</sub>C<sub>14</sub>を石油エーテルに溶解した溶液を、シリコン基板、石英基板、ガラス基板またはステンレスフォイル上に塗布した。これらの基板を水素炉に入れ、石油エーテルを蒸発させ、さらに440°CでSi<sub>6</sub>C<sub>14</sub>を熱分解させてシリコンを遊離させた。この結果、基板上にアモルファスシリコンの薄膜が形成されていることが確認された。また、加熱温度を上げることにより多結晶シリコンの薄膜を形成できることが確認された。

Si<sub>6</sub>C<sub>14</sub>を熱分解させてシリコンを遊離させた。この結果、基板上にアモルファスシリコンの薄膜が形成されていることが確認された。また、加熱温度を上げることにより多結晶シリコンの薄膜を形成できることが確認された。

【0076】また、実施例8と同様な方法を用いることによりp型またはn型のシリコン薄膜を形成できることが確認された。さらに、これらの方法を繰り返し、n型シリコン薄膜およびp型シリコン薄膜を積層してn-p接合を形成した結果、光起電力特性を示すことが確認された。

【0077】実施例10

シリコン源となるハロゲン化物として実施例8で用いたのと同一のSi<sub>5</sub>C<sub>12</sub>を用いた。このSi<sub>5</sub>C<sub>12</sub>を、融点近傍の温度で機械的操作により、シリコン基板、石英基板、ガラス基板またはステンレスフォイル上に塗布した。これらの基板を水素炉に入れ、石油エーテルを蒸発させ、さらに450°CでSi<sub>5</sub>C<sub>12</sub>を熱分解させてシリコンを遊離させた。この結果、基板上にアモルファスシリコンの薄膜が形成されていることが確認された。また、加熱温度を上げることにより多結晶シリコンの薄膜を形成できることが確認された。

【0078】また、実施例8と同様な方法を用いることによりp型またはn型のシリコン薄膜を形成できることが確認された。さらに、以上のようなシリコン薄膜の形成方法を繰り返して適用することにより多層のシリコン薄膜を形成し、図5に示す太陽電池を作製した。得られた太陽電池について、光起電力を測定して変換効率を求めた結果、14%であり、従来のアモルファスシリコン太陽電池に比べて遜色のない変換効率が得られることが確認された。

【0079】実施例11

シリコン源となるハロゲン化物として実施例9で用いたのと同一のSi<sub>6</sub>C<sub>14</sub>を用いた。このSi<sub>6</sub>C<sub>14</sub>を、融点近傍の温度で機械的操作により、シリコン基板、石英基板、ガラス基板またはステンレスフォイル上に塗布した。これらの基板を水素炉に入れ、石油エーテルを蒸発させ、さらに440°CでSi<sub>6</sub>C<sub>14</sub>を熱分解させてシリコンを遊離させた。この結果、基板上にアモルファスシリコンの薄膜が形成されていることが確認された。また、加熱温度を上げることにより多結晶シリコンの薄膜を形成できることが確認された。

【0080】また、実施例8と同様な方法を用いることによりp型またはn型のシリコン薄膜を形成できることが確認された。さらに、以上のようなシリコン薄膜の形成方法を繰り返して適用することにより多層のシリコン薄膜を形成し、図6に示す太陽電池を作製した。この素子においても、太陽電池特性が観測された。

【0081】実施例12

ゲルマニウム源となるハロゲン化物としてGe<sub>5</sub>C<sub>12</sub>

を用いた。この化合物は、石油エーテルなどの有機溶媒に溶解する。このGe<sub>5</sub>C<sub>112</sub>を石油エーテルに溶解した溶液を、シリコン基板、石英基板、ガラス基板またはステンレスフォイル上に塗布した。これらの基板を水素炉に入れ、石油エーテルを蒸発させ、さらに400°CでGe<sub>5</sub>C<sub>112</sub>を熱分解させてゲルマニウムを遊離させた。この結果、基板上に多結晶ゲルマニウムの薄膜が形成されていることが確認された。また、紫外線照射を加えて熱分解温度を下げた場合には、アモルファスゲルマニウムの薄膜を形成できることが確認された。

【0082】実施例13

シリコン源となるハロゲン化物としてSi<sub>5</sub>Br<sub>12</sub>を用いた。このSi<sub>5</sub>Br<sub>12</sub>を、融点近傍の温度で機械的の操作により、シリコン基板、石英基板、ガラス基板またはステンレスフォイル上に塗布した。これらの基板を水素炉に入れ、石油エーテルを蒸発させ、さらに400°CでSi<sub>5</sub>Br<sub>12</sub>を熱分解させてシリコンを遊離させた。この結果、基板上にアモルファスシリコンの薄膜が形成されていることが確認された。また、加熱温度を上げることにより多結晶シリコンの薄膜を形成できることが確認された。

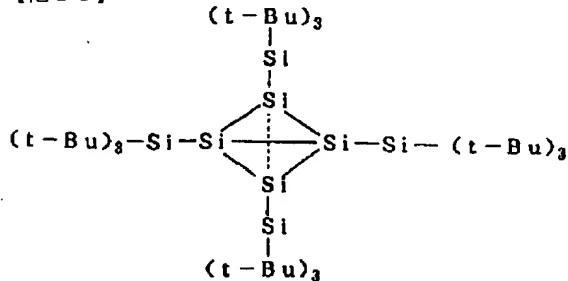
【0083】また、実施例8と同様な方法を用いることによりp型またはn型のシリコン薄膜を形成できることが確認された。さらに、以上のようなシリコン薄膜の形成方法を繰り返して適用することにより多層のシリコン薄膜を形成し、図6に示す太陽電池を作製した。この素子においても、太陽電池特性が観測された。

【0084】実施例14

シリコン源として下記化学式で示されるシラン系化合物をキシレンに溶解した溶液を、シリコン基板、石英基板、ガラス基板またはステンレスフォイル上に塗布した。これらの基板を水素炉に入れ、キシレンを蒸発させ、さらに650°Cでシラン系化合物を熱分解させてシリコンを遊離させた。この結果、基板上に多結晶シリコンの薄膜が形成されていることが確認された。

【0085】

【化15】



【0086】また、水素を2m<sup>2</sup>/minの流量で流して圧力を1atmに設定し、KrFエキシマレーザーを使用して10Jの出力で紫外線照射を加えて熱分解温度を350°Cに下げた場合には、アモルファスシリコンの

薄膜を形成できることが確認された。

【0087】次に、上記と同様な塗布工程の後、熱分解によりシリコンを遊離させる工程をジボランを含有する水素雰囲気中で実施した結果、p型シリコン薄膜を形成できることが確認された。また、上記と同様な塗布工程の後、熱分解によりシリコンを遊離させる工程をアルシンを含有する水素雰囲気中で実施した結果、n型シリコン薄膜を形成できることが確認された。なお、アルシンの代わりにホスフィンを用いてもよい。

【0088】さらに、以上のようなシリコン薄膜の形成方法を利用して図4に示す太陽電池を作製した。得られた太陽電池について、光起電力を測定して変換効率を求めた結果、8.5%であり、従来のアモルファスシリコン太陽電池に比べて遜色のない変換効率が得られることが確認された。

【0089】同様に、図5に示す太陽電池を作製した。得られた太陽電池について、光起電力を測定して変換効率を求めた結果、8.3%であり、従来のアモルファスシリコン太陽電池に比べて遜色のない変換効率が得られることが確認された。

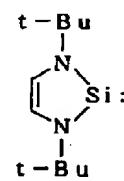
【0090】同様に、図6に示す太陽電池を作製した。この素子においても、太陽電池特性が観測された。

実施例15

シリコン源となる化合物として下記化学式で示されるシリレン系化合物、およびn型不純物源となる化合物としてP(SiMe<sub>3</sub>)<sub>3</sub>を用いた。これらの化合物の混合物のトルエン溶液を石英基板上にスピンドルコートした後、70°Cで1時間真空乾燥した。次いで、アルゴンと水素との混合気流下において、300°Cで1時間、600°Cで1時間加熱して、原料を熱分解させた。この結果、リンがドープされたシリコン薄膜が形成された。

【0091】

【化16】

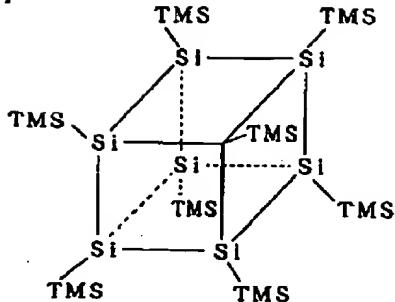


【0092】実施例16

シリコン源となる化合物として下記化学式で示されるトリメチルシリル基(TMS)を有するオクタシラキュバン化合物、およびn型不純物源となる化合物としてP(SiMe<sub>3</sub>)<sub>3</sub>を用いた。これらの化合物の混合物のトルエン溶液を石英基板上にスピンドルコートした後、70°Cで1時間真空乾燥した。次いで、アルゴンと水素との混合気流下において、300°Cで1時間、600°Cで1時間加熱して、原料を熱分解させた。この結果、リンがドープされたシリコン薄膜が形成された。

【0093】

【化17】



【0094】

【発明の効果】以上詳述したように本発明の方法を用いれば、半導体原料の溶液の塗布および熱分解という2つの工程を採用することにより、大面積のシリコンまたはゲルマニウムで構成される半導体薄膜を容易に形成でき、さらにこの方法を利用して大面積の太陽電池を製造できる。

## 【図面の簡単な説明】

【図1】本発明の方法を実施するための装置の一例を示す模式図。

【図2】本発明の方法を実施するための装置の他の例を示す模式図。

【図3】本発明の方法を実施するための装置のさらに他の例を示す模式図。

【図4】本発明の実施例において製造された太陽電池の一例を示す断面図。

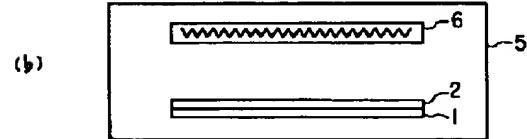
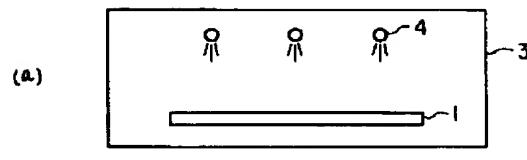
【図5】本発明の実施例において製造された太陽電池の他の例を示す断面図。

【図6】本発明の実施例において製造された太陽電池のさらに他の例を示す断面図。

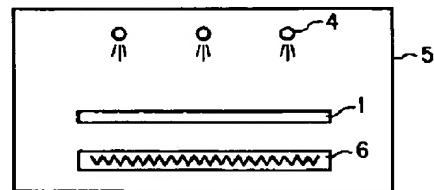
## 【符号の説明】

1 … 基板  
2 … 半導体薄膜  
3 … 塗布装置  
4 … ノズル  
5 … 水素炉  
6 … ヒーター  
7 … 原料容器  
8 … 半導体原料溶液  
10 1 … 供給ロール  
1 2 … 送りロール  
1 3 … 巻き取りロール  
2 1 … ガラス基板  
2 2 … 透明電極  
2 3 … p型アモルファスシリコン層  
2 4 … アンドープ (i型) アモルファスシリコン層  
2 5 … n型アモルファスシリコン層  
2 6 … アルミニウム電極  
2 7 … アルミニウム電極  
3 1 … ステンレス基板  
20 3 2 … モリブデン電極  
3 3 … p型アモルファスシリコン層  
3 4 … i型アモルファスシリコン層  
3 5 … p型アモルファスシリコン層  
3 6 … ITO電極  
3 7 … アルミニウム電極  
4 1 … アルミナ基板  
4 2 … SiO<sub>2</sub>膜  
4 3 … Si<sub>3</sub>N<sub>4</sub>膜  
4 4 … p型多結晶シリコン層  
30 4 5 … n型拡散層  
4 6 … ITO電極  
4 7 … アルミニウム電極

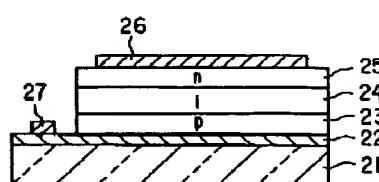
【図1】



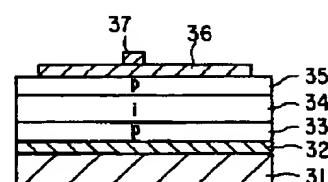
【図2】



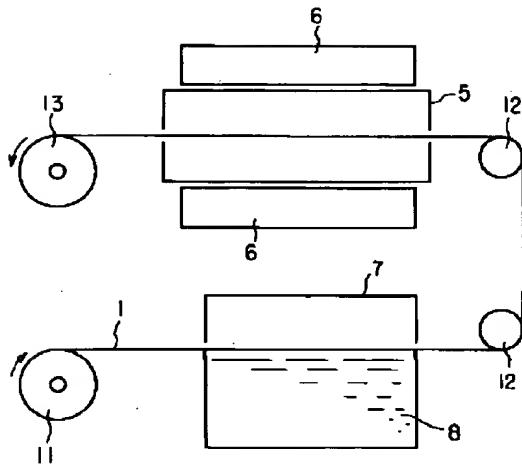
【図4】



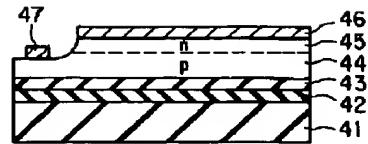
【図5】



【図3】



【図6】



フロントページの続き

(72)発明者 鎌田 敦之  
神奈川県川崎市幸区小向東芝町1番地 株  
式会社東芝研究開発センター内

(72)発明者 佐野 健二  
神奈川県川崎市幸区小向東芝町1番地 株  
式会社東芝研究開発センター内